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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

NOTES ON TAKA-DIASTASE.

BY W. E. STONE AND H. E. WRIGHT.

Received July 8, 1898.

THERE has recently come into notice, chiefly through its industrial applications, a starch-saccharifying enzyme of apparently unusual value. This substance, called taka-diastase, has been in use in Japan for an indefinite time in the production of alcoholic beverages in much the same capacity as that for which we employ malt. Its introduction to America is due to Mr. Jokichi Takamine, who for some years has been occupied in furthering its application in the distilling industry in the United States. Pharmaceutical preparations of this enzyme intended for the relief of amylaceous indigestion, are also on the market. So far as the writers are informed neither the material itself nor its action on starch has been much studied from the purely scientific side or, if such investigations have been made, they have not been generally published. It seemed a matter of interest, therefore, to endeavor to secure definite information regarding such a valuable and interesting material.

Mr. Takamine has recently described[1] the patented method for preparing the material, a résumé of which will be appropriate here. Taka-diastase is, so far as known, somewhat similar to malt-diastase in its chemical character; *viz.*, a highly

[1] *Am. J. Pharm.*, 70, No. 3; *J. Soc. Chem. Ind.*, 17, No. 2.

nitrogenous substance, readily soluble in water and dependent upon certain conditions of temperature for its maximum activity. Its action is also affected by alkalies and acids. It is produced as the result of the growth of a species of mould (*Eurotium Oryzae* Ahlberg), upon rice, maize, wheat bran, etc. For its production, as at present practiced in this country, wheat bran is steamed and, after cooling, is sown with the spores of the fungus. After twenty-four hours in culture-rooms at a temperature of about 25° C. the fungus growth becomes visible. In forty or fifty hours the content in diastatic material has reached the maximum and further growth of the fungus is checked by cooling. The material, now consisting of the bran felted together with fungus mycelium, is called "taka-koji."

It may be mixed with grain or starchy materials in the same manner as malt is used, and, like malt, will speedily convert the starch into fermentable sugars. An aqueous extract of the mass may be used for a similar purpose. For the preparation of a pure product, which however is not necessary for ordinary industrial purposes, the aqueous extract is concentrated by evaporation and on the addition of alcohol the diastatic substance may be precipitated as a yellowish powder, easily soluble in water, of stable keeping qualities and possessed of an unusual power of converting starch into sugar. The medicinal preparation above mentioned is obtained in this way and represents a fairly pure form of the diastatic principle. This bears the name of "taka-diastase."

This paper presents the results of some observations upon the action of taka-diastase upon starch as compared with the ordinary diastase of malt.

For the purposes of this comparison, taka-diastase was employed which was kindly furnished by the makers, Messrs. Parke, Davis & Co., of Detroit, Mich. The malt-diastase was prepared in the laboratory by digesting fresh pale malt with water at room temperature during three or four hours, filtering and adding to the clear filtrate two volumes of strong alcohol. The flocculent precipitate was collected, pressed dry, and finally dried in desiccators over sulphuric acid.

A series of experiments was carried out in which pure potato starch, which had been changed to paste by boiling, was sub-

jected to the action of the two sorts of diastase. Three methods were employed to determine the degree to which the starch had been changed; *viz.*, first, the iodine test; second, the optical behavior of the solution; third, the determination of the actual amounts of sugar produced.

In every case care was taken to preserve uniform conditions except as specified below.

1. Comparative action of the two kinds of diastase on potato starch as indicated by the iodine test.

a. Four samples of starch of one-half gram each were boiled with fifty cc. of water each. To two were added 0.05 gram malt-diastase each and they were kept at 60° C. throughout the test. To the other two were added 0.05 gram taka-diastase and these were kept at 40° C. throughout the test. At fixed intervals the solutions were tested with iodine for the presence of starch, in the following manner: Three drops of the solution were removed to a white test plate and were mixed with one drop of standard aqueous iodine solution containing one and a half grams potassium iodide and eight-tenths gram iodine in one liter. The least trace of starch is indicated under these conditions by a blue or greenish tint or as the starch is passing through some of the preliminary stages of conversion the tint will be more or less violet or purple. In this and other experiments the duplicate samples were found to agree very closely in their behavior.

The results of the observations were as follows:

End of six minutes: Malt-diastase, no perceptible change; taka-diastase, deep violet color.

End of twelve minutes: Malt-diastase, reddish brown; taka-diastase, violet to reddish.

End of eighteen minutes: Malt-diastase, light brown or yellow due to iodine solution; starch reaction had disappeared; taka-diastase, light violet or reddish.

End of forty-five minutes: Taka-diastase, light violet tint.

End of sixty minutes: Taka-diastase, light greenish-blue tint, evidently containing small traces of unchanged starch.

b. The proportions of starch to diastase were increased, in other respects the conditions remaining the same as in "*a*". Four samples of starch of one gram each, converted to paste by

boiling with fifty cc. of water, received diastase of each kind as above.

End of six minutes: Malt-diastase, deep violet; taka-diastase, deep reddish violet.

End of twelve minutes: Malt-diastase, reddish violet; taka-diastase, deep reddish violet.

End of eighteen minutes: Malt-diastase, reddish brown; taka-diastase, light reddish violet.

End of twenty-seven minutes: Malt-diastase, light brown, no starch reaction; taka-diastase, slightly reddish violet.

End of six hours: Taka-diastase, still a bluish green color showing small amounts of unchanged starch.

c. The proportions of starch to diastase were again increased. Four samples of two and a half grams each of starch were converted to paste in 250 cc. of water and received respectively 0.05 gram malt- or taka-diastase.

End of six minutes: Malt-diastase, no perceptible change; taka-diastase, deep reddish violet.

End of twelve minutes: Malt-diastase, deep reddish violet; taka-diastase, deep reddish violet.

End of forty-five minutes: Malt-diastase, brownish yellow color, no further starch reaction; taka-diastase, light violet or greenish tint.

End of twelve hours: Taka-diastase, still showed the bluish-green tint.

d. The amounts of diastase were diminished. Four samples of starch of 1.875 grams each in forty cc. of water, received respectively 0.025 gram of taka- or malt-diastase.

End of six minutes: Malt-diastase, deep blue, little or no change; taka-diastase, deep reddish violet.

End of twelve minutes: Malt-diastase, reddish brown; taka-diastase, deep reddish violet.

End of twenty-four minutes: Malt-diastase, yellowish brown color, no starch reacting; taka-diastase, reddish violet.

End of forty-five minutes: Taka-diastase, still gives a violet tint.

e. Four samples of starch of two and a half grams each in 250 cc. water with 0.025 gram respectively of malt- or taka-diastase.

End of six minutes: Malt-diastase, no change; taka-diastase, deep reddish-violet.

End of twelve minutes: Malt-diastase, deep reddish brown; taka-diastase, deep reddish brown.

End of twenty-four minutes: Malt-diastase, yellowish brown, no starch reaction; taka-diastase, deep reddish brown.

End of sixteen hours: Taka-diastase, still gave a bluish drab color.

In every case it was apparent to the observer that the effect of the taka-diastase was more rapid at the outset, as indicated by the almost immediate change from the typical blue of the starch iodine compound to reddish and violet tints. It was generally noticeable also that the taka-diastase liquefied the starch paste very rapidly, more so than the malt-diastase. On the other hand, the complete conversion of the starch into forms which no longer gave color reactions with iodine was effected much earlier by the malt-diastase, while the taka-diastase scarcely attained this result after several hours.

2. Comparative action of the two kinds of diastase on potato starch as shown by optical tests.

The different conversion products of starch exhibit varying degrees of optical activity. The dextrines possess a high specific rotation usually stated as approximately 190°. Maltose has the specific rotation 130°–140°, while the ultimate conversion product, dextrose, has the specific rotation 52.5°.

In considering the action of diastase, however, maltose may be regarded as the ultimate product, and Brown and Morris have pointed out[1] that the optical behavior of a solution of the products of diastatic action on starch paste, is that of a mixture of maltose and dextrose. A determination, therefore, of the specific rotation of such a solution gives information regarding the degree of conversion of the starch. The degree of completeness of the change from starch through dextrines of high specific rotation to maltose of a lower rotatory power will be indicated by a diminution of the specific rotation. A few qualitative observations along this line were made as follows:

Eight samples of starch of equal weight were converted to paste by boiling in equal amounts of water; to each of four were added

[1] *Chem. News*, 71, 123.

0.05 gram malt-diastase and to the other four 0.05 gram taka-diastase each. These samples were kept respectively at 60° and 40° C. At regular intervals one of each series was withdrawn, heated quickly to boiling to check further action of the diastase, cooled, and made up to a volume of 100 cc. The specific rotation was then determined in a Laurent polarimeter with sodium light. Two series of experiments were made in this way, using different amounts of starch.

a.

One-half gram starch in 100 cc. water.
0.05 gram of diastase.

	Malt-diastase at 60° C.		Taka-diastase at 40° C.	
Time. Hours.	Observed rotation.	Specific rotation.	Observed rotation.	Specific rotation.
¼	1°20′	133°20′	1°15′	125°
½	1°19′	131°40′	1°13′	121°40′
1	1°19′	131°40′	1°9′	115°
2	1°19′	131°40′	1°7′	111°40′

b.

One gram starch in 100 cc. water.
0.05 gram of diastase.

	Malt-diastase at 60° C.		Taka-diastase at 40° C.	
Time. Hours.	Observed rotation.	Specific rotation.	Observed rotation.	Specific rotation.
¼			2°47′	139°20′
½	2°57′	147°30′	2°43′	135°50′
1	2°45′	137°30′	2°29′	124°10′
2	2°47′	139°20′	2°27′	122°30′

The products of the action of taka-diastase were in all cases of lower specific rotation than those from malt-diastase, indicating a more rapid change to maltose.

3. Comparative action of the two kinds of diastase on potato starch as indicated by the amount of sugar formed.

The most practical as well as most conclusive test of the relative degree to which starch has been converted by diastatic action is that of actually determining the amount of sugar formed under comparative conditions. This has been done as follows:

Several equal samples of the starch were boiled with equal volumes of water to change into paste, were cooled to the proper temperature, and received respectively given amounts of one or

the other diastase. At the expiration of a given time one sample of each kind was withdrawn, boiled to check the action of the diastase, cooled, and filled up to definite volume. The amount of sugar present was determined by the method described by Defren.[1]

It is believed that these results form a very good basis for comparing the actual efficiency of the two enzymes for a given time.

a.

One-half gram starch. 100 cc. water. 0.05 gram diastase.

	Malt-diastase at 60° C.			Taka-diastase at 40° C.		
Time.	Cupric oxide from 10 cc.	Maltose.	Total maltose from 5 grams starch.	Cupric oxide from 10 cc.	Maltose.	Total maltose from 5 grams starch.
Hours.		Mg.	Mg.		Mg.	Mg.
¼	39.5	29.0	290	61.4	44.3	443
½	41.1	29.7	297	63.9	46.5	465
1	40.7	29.7	297	65.8	47.9	479
2	40.2	29.0	290	73.0	53.0	530

b.

One gram starch. 100 cc. water. 0.05 gram diastase.

	Malt-diastase at 60° C.			Taka-diastase at 40° C.		
Time.	Cupric oxide from 10 cc.	Maltose.	Total maltose from 1 gram starch.	Cupric oxide from 10 cc.	Maltose.	Total maltose from 1 gram starch.
Hours.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
¼	71.4	51.6	516	84.5	61.8	618
½	84.7	61.8	618	99.6	72.8	728
1	75.5	55.2	552	120.1	87.4	874
2	85.5	61.8	618	143.6	105.0	1050

These results show that for a given short time the actual saccharifying power of the taka-diastase is decidedly superior to the malt-diastase.

4. The use of taka-diastase as an analytical reagent for the determination of starch.

Malt-diastase has come to be most favorably looked upon as an agent for the selective removal and analytical determination of starch occurring in grains and vegetable materials, associated with other carbohydrates. One drawback to its common use is its unstable character in the isolated form, since it is well known

[1] This Journal, 18, 749.

that preparations of diastase rapidly deteriorate and lose their value. On this account the practice is to freshly prepare aqueous infusions of malt for immediate use in starch determination. Such infusions, however, always contain sugar, which being added to the analytical sample necessitates a subsequent correction. The use of malt-diastase in any form therefore as an analytical reagent is more or less tedious and renders welcome any substitute which would avoid these objections and at the same time act as an efficient starch solvent. Taka-diastase has seemed a promising substance for this purpose, although the qualitative tests described under "1" indicate that it does not readily effect complete conversion of starch under the conditions stated.

The following experiment upon materials commonly presented for starch determinations is instructive:

One gram each of air-dried, finely ground wheat, maize, and potato were heated to the boiling-point during thirty minutes with fifty cc. of water. After cooling to 60° C., ten cc. of malt infusion were added to each and the temperature was carefully maintained as above. To each of a similar series prepared in the same way was added 0.05 gram and to each of another similar series 0.1 gram of taka-diastase: these samples were kept at 40° C. At the expiration of four and one-half hours all were subjected to the iodine test for starch. In those treated with malt infusion all traces of starch had disappeared from the potato while the wheat and maize still showed slight traces of starch under the microscope. In those treated with taka-diastase, all, without exception, showed an abundance of unchanged starch, nor was there apparently any sharp distinction between the samples of the same material receiving different amounts of the diastase.

After seven hours the samples treated with malt-diastase gave no further indication of starch. But all of those treated with taka-diastase gave pronounced starch reactions. Additional treatment during twelve hours at ordinary temperature did not suffice to remove all of the starch from the latter samples.

Evidently these results were unfavorable to the employment of taka-diastase as a reagent but a quantitative comparison was

made as follows: Duplicate, two-gram samples of air-dried, ground wheat were weighed and gelatinized by boiling thirty minutes with 100 cc. of water. To one was added twenty cc. of a malt infusion made by digesting five grams of malt in fifty cc. of water three hours at ordinary temperature; this sample was then kept at 60° C. To the other duplicate was added 0.05 gram taka-diastase and the temperature kept at 40° C.

After four hours the solutions were filtered. The residue from the wheat treated with malt infusion proved to be free from starch when examined under the microscope after treatment with iodine solution. The wheat treated with taka-diastase was slightly stained blue when treated with iodine. The filtrates received each ten cc. concentrated hydrochloric acid and were heated in boiling water during one hour. After cooling, neutralizing, and making up to volume, the amount of sugar in each was determined by titration with Fehling's solution and the results calculated to starch in the original samples of wheat.

The treatment with malt infusion gave 55.46 per cent. of starch. The treatment with taka-diastase gave 52.94 per cent. of starch.

This result agrees wholly with the qualitative experiments previously made and indicates that under the stated conditions taka-diastase is not adapted for use in the quantitative determination of starch. It is nevertheless possible that some modification of these conditions or of the material itself may lead to more satisfactory conclusions as the result of some future investigation.

It is certain, however, that in gross industrial operations the cheapness and stability of taka-koji and taka-diastase will commend it while its ability to convert a very large proportion of the starch present in a grain into sugar within a very short time should render it a very valuable substitute for malt. The application of taka-diastase as an aid to starch digestion is doubtless of high value by reason of its convenience, its notable saccharifying power, and its permanent keeping qualities.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 1.]

THE ACTION OF ORGANIC ACIDS UPON NITRILS.[1]

BY JOHN ALEXANDER MATHEWS.

Received July 7, 1898.

THE action of organic acids upon nitrils has been the subject of a number of investigations which have been reported from this laboratory at intervals during the past seven years. The nitrils and acids employed in the various experiments have been made to react under the influence of elevated temperature and pressure in sealed tubes. In nearly every instance a few drops of acetic anhydride have been added to the mixtures of acids and nitrils to insure anhydrous conditions within the tubes. This precaution is believed to increase the yield of the principal products of the reaction. The reaction between acetic acid and acetonitril, whereby Gautier found diacetamid to be produced,[2] suggested to Colby the idea of trying parallel reactions between other acids and nitrils. Colby and Dodge[3] experimented with a large number of monobasic acids and mononitrils of both the fatty and the aromatic series. Their results show that under conditions of heat and pressure :

I. Fatty nitrils and fatty acids yield secondary amids.

II. Fatty nitrils and aromatic acids yield fatty acids and aromatic nitrils.

III. Aromatic nitrils and fatty acids give mixed secondary amids.

IV. Aromatic nitrils and aromatic acids give secondary amids. One exception was noted under the fourth head by these authors.

Not so much work has been done upon dibasic acids. Miller[4] and Seldner[5] worked with fatty dibasic acids, the former with succinic and the latter with glutaric acid. They proved that the imids of these acids result under three different conditions. From

I. Dibasic acid and acetonitril.

[1] Read at the meeting of the New York Section, May 6, 1898.

[2] *Ztschr. anal. Chem.*, *1869*, p. 127, or *Compt. rend.*, 60, 1255.

[3] *Am. Chem. J.*, 13, 1.

[4] This Journal, 16, 443.

[5] *Am. Chem. J.*, 17, 532.

II. Dinitril and acetic acid, and

III. Equal molecules of the dibasic acid and its nitril.

Two years ago the author published his first experiments upon aromatic dibasic acids. Phthalic acid was first tried and its imid resulted by heating it with propionitril. In the following pages are given results obtained recently along the same line of experimentation. This work may be grouped under two heads. First, experiments with monobasic acids, simple and substituted; second, experiments with aromatic, polybasic acids.

PART I.

UPON THE ACTION OF FATTY NITRILS ON MONOBASIC AROMATIC ACIDS, WITH A PRELIMINARY NOTE ON MALONIMID.

Before describing the experiments upon aromatic acids which compose the main part of this investigation, a few words upon some attempts to prepare the unknown imid of malonic acid may not be out of place, since in these attempts the methods employed were the same as those used in making the imids of the bibasic aromatic acids.

Malonic Acid and Ethylene Cyanide.—Two tubes containing equal molecules of malonic acid and ethylene cyanide were made by Miller in 1893. The first tube, when heated, exploded at 196° C. The second one was heated at 150° C. for five and one-half hours. This tube was set aside and when examined by me recently it was found that the contents were liquid and brown. Very strong outward pressure was noticed upon unsealing. Succinimid was found but no malonimid seems to have been produced. Malonic acid loses part of its carbon dioxide readily by heating, and for this reason it was thought better to use malonitril and treat it with glacial acetic acid. This method was unsatisfactory, too, for almost complete decomposition took place by heating. As throwing some light upon the question of the rearrangement of cyan acids to give imids, the next experiments were made upon cyanacetic acid. This acid was heated to 190° in benzol medium. There was strong pressure upon opening and the contents of the tube were evaporated upon the water-bath to drive off the benzol. The residue was extracted with absolute alcohol. This solution was treated with boneblack and by evap-

oration nearly to dryness and long standing a small amount of crystalline material separated. This was pressed and dried and recrystallized. It was soluble in acetone, ether, alcohol, and water, and almost insoluble in benzol. Its melting-point was 115° C. It gave a nitrogen test and was neutral in its reaction with litmus paper. By boiling with potassium hydroxide solution, acidifying and evaporating to dryness, and extracting with absolute alcohol, an acid was obtained melting at 130°, very soluble in water and alcohol. This seems to be malonic acid. It seems probable, therefore, that malonimid was produced by the rearrangement of the cyanacetic acid. Not enough of this supposed imid has as yet been obtained to make a thorough investigation, but the same material was obtained from two tubes made up and heated at different times and its further study will be interesting.

Benzoic Acid and Ethylene Cyanide.—Two sealed tubes containing ethylene cyanide and benzoic acids and a drop or two of acetic anhydride were prepared. The first contained equal molecules and the second contained two parts of acid to one part of nitril. Both were heated seven hours at 145° C. and then five and a half hours at 195° C. The contents were then black and semi-solid and crystalline. In the first tube benzonitril was found. The contents of the tube were treated with weak sodium carbonate solution and then evaporated to dryness and extracted several times with ether. The operations thus far described were carried out by Dr. E. H. Miller, in 1893. The ether extract gave a white crystalline solid upon evaporation. This residue was very soluble in acetone. After recrystallization from water and twice from acetone, succinimid, melting at 124° C., was obtained in characteristic crystals. These were tested for nitrogen and it was found.

The second tube contained originally three grams of ethylene cyanide and 9.15 grams of benzoic acid; *i. e.*, two molecules of acid to one of nitril. No pressure was observed upon opening. A strong odor of benzonitril was at once apparent. The tube contents were liquid at the temperature of a hot water-bath and were poured into dilute sodium carbonate solution. From results obtained by Colby and Dodge and by Miller, it was

thought that this tube might contain benzoic acid, ethylene cyanide, benzonitril, succinic acid, succinimid, and dibenzamid. Dibenzamid and succinic acid were not found. Colby and Dodge showed that by heating together benzoic acid and acetonitril at 250°–260° C. there was formed principally benzonitril and acetic acid. At about the same temperature benzonitril and benzoic acid combine to give dibenzamid. In our tube probably the temperature had not been carried high enough to produce this condensation. The primary reaction which seems to have taken place in both tubes is :

$$C_6H_5COOH + C_2H_4(CN)_2 = C_6H_5CN + C_2H_4(CO)_2NH.$$

The second tube was examined as follows : Upon pouring the contents into sodium carbonate solution three and one-half cc. of black liquid material separated at the bottom. This was drawn off by means of a separatory funnel and showed to be benzonitril. It was distilled with steam, separated from the water, partly dried by evaporation upon a water-bath, and then with small fragments of calcium chloride. The once purified product boiled at 188° (uncorr.). The boiling-point of benzonitril is given as 191° C.

The sodium carbonate solution was evaporated to dryness and extracted with ether and then with water. The ether extract gave a residue upon evaporation which was succinimid. Recrystallized from acetone it gave oblong, colorless crystals (melting-point 125° C.).

The water extract above mentioned by acidifying with hydrochloric acid gave a bulky precipitate. This, filtered off, washed, and dried, melted at 117.5°. It was unchanged benzoic acid. Recrystallized from hot water, large plates were deposited (melting-point 120° C.). These crystals are sublimable at the temperature of boiling water. 2.75 grams of benzoic acid were recovered, which is also about the amount of benzonitril produced. After the ether and water extractions of the original tube contents, a large, charred, carbonaceous residue and a little tarry matter, believed to be partly ethylene cyanide, remained.

In Miller's dissertation upon succinimid are reported a number of attempts to prepare β-cyanpropionic acid in sufficient quantities to try whether it could be made to rearrange into its

isomer, succinimid. It seems to me that these two experiments point to the formation of β-cyanpropionic acid as an intermediate product. Either it must be considered that the carboxyls of the benzoic acid change places with both nitril groups of one-half of the ethylene cyanide or with one of the nitril groups forming β-cyanpropionic acid, which rearranges into succinimid. Of course, if the first assumption is the correct one, the succinic acid formed would react with the unchanged ethylene cyanide and two molecules of succinimid would result as shown by Miller. It seems probable that had succinic acid been formed in either of these experiments some of it would have been found, for these reactions are not often complete. On the other hand, if β-cyanpropionic acid were the intermediate product we should not expect, because of its well-known instability, to find it withstanding a temperature of 195° unchanged. Only about one gram of succinimid was produced and this fact, together with the large amounts of decomposition-product, seems to strengthen the second assumption in regard to the course of the reaction.

Phenylacetic Acid and Ethylene Cyanide.—Two tubes, the first containing equal molecules of phenylacetic acid and the second two molecules of acid to one of nitril, were prepared by Miller in 1893. Both tubes were heated for six hours at 150° C. The contents were then black and semi-fluid. Not much outward pressure was noticed upon opening. These tubes were set aside and not examined until 1898. The reaction in tube I seems to be:

$$C_6H_5.CH_2.COOH + C_2H_4(CN)_2 = C_6H_5CH_2.CN + C_2H_4(CO)_2NH.$$

Phenylacetamid was also found in this tube and its presence cannot be explained except by the presence of some water in the tube which reacted upon the phenylacetonitril. The reaction of tube II was primarily the same as in I. The excess of phenylacetic acid then reacted with the phenylacetonitril and produced diphenyldiacetamid:

$$C_6H_5.CH_2.COOH + C_6H_5.CH_2.CN = (C_6H_5.CH_2.CO)_2NH.$$

No phenylacetamid was found in this experiment, but some phenylacetic acid was recovered.

Tube I was examined as follows: The contents were extracted with warm water. A black, oily residue was left. This proved to be impure phenylacetonitril. The water extraction was of a light yellow color and, by cooling, it gave crystals. These were flat plates melting at 155° C. They were found to contain nitrogen and, by boiling with hydrochloric acid and cooling, crystals of phenylacetic acid were deposited (melting-point 76° C.). A second crop of the crystals melting at 155° was obtained by concentrating the mother-liquor. These crystals were phenylacetamid. By evaporating the second mother-liquor nearly to dryness succinimid was found. This, recrystallized from acetone, melted at 124° C.

Tube II was examined in about the same way. The water extract by cooling gave no phenylacetamid. Upon concentration some phenylacetic acid separated and later succinimid was found. The black oily residue from the water extraction was soluble in hot alcohol. It was treated with boneblack and then upon cooling, needle crystals melting at 190° C. were obtained. These were recrystallized and deposited as slender filament-like needles, melting at 192°. They were insoluble in water and seemed to be diphenyldiacetamid, described by Colby and Dodge. The alcohol solution, after filtering off the diphenyldiacetamid, was distilled. The high-boiling fraction was caught separately and dried. The boiling-point of the benzyl cyanide thus obtained was 230° C.

It will be noticed that these results are parallel to those obtained with experiments with benzoic acid. The two series of experiments form a connecting link between the work of Colby and Dodge upon monobasic acids and their nitrils, and the work of Miller upon succinimid, and serve to confirm in several points the reported results of these chemists.

Salicylic Acid and Acetonitril.—Equal molecules of salicylic acid and acetonitril were heated five hours at 195°–200° C. No reaction seems to have taken place, unchanged salicylic acid being the only solid product. This experiment repeated at 215°-230° always gave a reddish liquid. Great pressure was noted in these last experiments and carbon dioxide was the principal gas evolved. Phenol was shown to be present in every case. No other products were identified. The tube contents were partly

soluble in water and the insoluble portion consisted of a sticky, thick liquid substance. The water solution by cooling gave a few clusters of crystals, melting at 137°–138°, after recrystallization. These gave no nitrogen reaction. The first reaction seems, then, to result in the formation of phenol, and unidentified products mentioned above do not result by any action of a nitril upon an acid. The investigation was, therefore, discontinued for the present and will be resumed later.

Anthranilic Acid and Acetonitril.—Anthranilic acid and acetonitril were heated together in equal molecules for five hours at 220°–230° C. Very strong pressure was observed upon opening the tubes and the gases evolved consisted mainly of carbon dioxide. The tube contents were evaporated to dryness upon a water-bath. The black residue was almost entirely soluble in hot water. This solution upon cooling gave fine needle-like crystals (melting-point 230° C.). These, treated with boneblack and recrystallized, melt at 232° C. and may be sublimed. By boiling them with strong hydrochloric acid and cooling, long needles result, which do not melt at 280° C. but sublime. This material was not identified nor were the few drops of liquid (boiling-point 240°), which were isolated in one of the experiments. This liquid did not give a test for anilin with bleach solution but gave a deep brown color when so treated. On account of the partial decomposition taking place within the tubes, no further investigations upon anthranilic acid and acetonitril were made, but the reaction will be made the subject of future study.

PART II.

UPON THE ACTION OF FATTY NITRILS UPON AROMATIC POLYBASIC ACIDS.

Phthalic Acid and Propionitril.—In a number of reactions which I have tried phthalimid resulted. The first of these experiments was made in 1896.[1] This series of experiments is explained by the following reaction :

$$C_6H_4(COOH)_2 + C_2H_5CN = C_6H_4(CO)_2NH + C_2H_5COOH.$$

The tubes were made up containing both one and two molecules of nitril to one molecule of phthalic acid. The best

[1] This Journal, 18, 679.

results, so far as the production of phthalimid was concerned, were obtained by heating equal molecules of the reagents at 180°–200° for a period of five and a half hours. The yield was ninety-two per cent. of the theoretical. The reaction seems to be practically completed in three and a half hours, for one tube heated thus yielded eighty-eight per cent. The crystalline product in these tubes was washed with a little dilute sodium carbonate solution to remove phthalic and propionic acids and any nitril remaining. The crystals remaining melted at 228° C. Portions recrystallized from alcohol, acetic acid, and alcohol with the addition of boneblack, melted a little higher, 229.5°–230° C. These crystals gave off ammonia by boiling with potassium hydroxide. By standing with concentrated ammonium hydroxide they were converted into phthalamid, microscopic needles melting at 217.5° (uncorrected). The amid is decomposed by boiling, giving off ammonia gas, and phthalimid crystallizes out again upon cooling.

Phthalic Acid and Ethylene Cyanide.—Equal molecules of phthalic acid and ethylene cyanide were heated together. Two tubes received four hours' heating at 220°–223°. Upon opening, strong outward pressure was noticed, and the contents of the tubes were black and charred. Thinking that succinimid might be present, the tube contents were extracted with water. This solution upon evaporation gave a small amount of material, very soluble in methyl or ethyl alcohol and acetone, difficultly soluble in benzol. It crystallized in needles (melting-point 165°–167°), and gave nitrogen test by boiling with alkali. By boiling with hydrochloric acid, crystals were obtained which melted above 200° with decomposition. The residue, after cooling, melted at 127° and sublimed in fine needles. This seems to be phthalic acid. The hydrochloric acid solution, after filtering off the above crystals, was shaken up with ether. The ether solution, by evaporation, gave a small residue (melting-point 183°–185)°, which corresponds with succinic acid and when boiled with sulphuric acid and alcohol gave an odor of succinic ester. The solution, after extracting with ether, was evaporated to dryness, dissolved in a little water and a platinic chloride test made for ammonia. The precipitate which was obtained was tested to make sure that no fixed alkalies were present. Unfortunately,

the amount of this substance produced was too small for further investigation or analysis. The above tests, however, would indicate that the compound might be a double imid of phthalic and succinic acids. The second tube contained also a little of this material, having the same properties as before, but its melting-point was found to be a little higher, 170° C.

In a third tube, run as nearly as possible like these two, for the purpose of obtaining enough of this peculiar compound to analyze, none of it was found. In tube I no succinimid was found, but there was a great deal of phthalimid. In tubes II and III succinimid and phthalimid were found, the former in very small quantities. In all the tubes was found considerable black, charred, insoluble residue.

Tube IV was heated to 200° for five hours. Upon examination succinimid, phthalimid, and unchanged phthalic acid were found. In tube II the contents were moist and an attempt was made to filter off the solid portion by using a hot water funnel. The funnel was covered with a watch-glass and the vapors which arose from the funnel deposited upon the cover glass, white crystals, which upon drying and recrystallizing, proved to be succinimid. The reaction which works then to some extent in these experiments is:

$$C_6H_4(COOH)_2+C_2H_4(CN)_2 = C_6H_4(CO)_2NH+C_2H_4(CO)_2NH.$$

III. *Phthalic Anhydride and Acetonitril.*—When acetic anhydride and acetonitril are heated at 200° there is found triacetamid, $(CH_3CO)_3N$. To see if a similar reaction would take place between phthalic anhydride and acetonitril giving acetylphthalimid, these reagents were heated together in equal molecules, and also with excess of nitril, but in neither case was acetylphthalimid formed. According to Aschan[1] acetylphthalimid is produced when phthalimid is boiled for several hours with acetic anhydride in a flask with return condenser, thus:

$$C_6H_4(CO)_2NH + (CH_3CO)_2O = C_6H_4(CO)_2N.OC.CH_3 + CH_3.COOH.$$

Acetylphthalimid is easily decomposed by hot water or alcohol and by cold alkali. Aschan notes that the imid hydrogen does not readily submit to replacement by acid radicals.

[1] *Ber. d. chem. Ges.*, 19, 1400.

In my experiments tube I, containing equal molecules, was heated four hours at 145° C., and then four and a half hours at 195°–200° C. Upon examining the tube contents phthalic anhydride and phthalimid were found. The latter should not have resulted had the reagents used not contained moisture. Tube II received the same treatment as I and four hours additional at 225°–235° C. It showed no apparent change over tube I and was unsealed, more nitril added, and after resealing it was heated again at 200°–210° for five hours. Phthalimid was again found, together with acetic acid and unchanged phthalic anhydride. Tube III was made up as the other two except that the nitril used was twice distilled over phosphorus pentoxide. In this tube no reaction took place, except that a little imid was again found. The reaction expected seems therefore not to have worked under the conditions presented.

Terephthalic Acid and Propionitril.—Under the same conditions which gave phthalimid from *o*-phthalic acid and propionitril, no reaction takes place with *p*-phthalic acid, neither is any reaction obtained at a much higher temperature, 260° C. The tube contents, after heating, are completely soluble in dilute carbonate solution, except that at the higher temperatures a little tarry substance may remain. The solid contents do not give a nitrogen test and *p*-phthalic acid is recovered quantitatively by acidifying the sodium carbonate solution with hydrochloric acid.

Homophthalic Acid and Acetonitril.—The experiments with homophthalic acid and acetonitril, looking to the production of homophthalimid, were not entirely successful because of the small quantity of homophthalic acid obtainable. In but one instance was any product found resembling homophthalimid. This is rather surprising, inasmuch as the ammonium salt of this acid gives an imid by heating, and every other acid whose imid results in this way and that has been tried by our nitril reaction has given an imid. After five hours' heating of equal molecules of homophthalic acid and acetonitril at 190° C. and extracting the tube contents with carbonate solution, a small residue remained. Upon dissolving this in hot acetic acid and cooling, crystals were obtained which do not entirely melt, but darken, and give off a brown liquid at 230° C., leaving a charred residue. The crystals contain no nitrogen. The mother-liquor

from them by concentration gave a few crystals which contain nitrogen and melt, after drying between filter-papers, at 215°. A third crop of crystals filtered off, washed, and dried, were light brown, contained nitrogen, and melt at 230°–232°, darkening before melting. These answer to the description of homophthalimid. The amount of this product was very small and nothing like it was isolated in two subsequent similarly conducted experiments. In all of them, however, the material not containing nitrogen and decomposing above 230° into a brown liquid and charred residue was found.

A peculiar compound very insoluble in cold alcohol and acetic acid and soluble in ammonia, was found. Its melting-point was indefinite, but by heating it left a residue infusible at 285° C. It crystallizes in fine filament-like crystals, which are snow-white and pack down to a spongy, felt-like mass of a texture which makes it scarcely visible upon the filter-paper. It contains no nitrogen and not enough of it was obtained to analyze.

Cyan-*o*-toluic acid did not rearrange by heating under pressure in benzol at 190° C. to yield its isomer, homophthalimid. In this regard it differs from *o*-cyanbenzoic acid, which so readily changes into phthalimid. An ether solution of the tube contents in one of these experiments gave a few long needle-shaped crystals, melting at 182° C. They contained nitrogen but were not identified.

Gabriel[1] states that cyan-*o*-toluic acid does not rearrange to give an imid but does not mention under what conditions the experiment was tried to produce this change. He concludes that when the cyanogen group is on the ring, rearrangements may be expected as was just mentioned of *o*-cyanbenzoic acid. In proof of this he shows that by acting upon orthocyanbenzyl cyanide with fuming hydrochloric acid at 100° for one hour homophthalimid is produced. He explains this by considering that the cyan group of the side chain is more reactive than the cyan group on the ring, hence *o*-cyanphenylacetic acid is first formed and this rearranges to give homophthalimid. That is:

$$C_6H_4\begin{cases}CH_2CN\\CN\end{cases} + HCl + 2H_2O = C_6H_4\begin{cases}CH_2COOH\\CN\end{cases} + NH_4Cl$$

[1] *Ber. d. chem. Ges.*, 20, 2502.

and $C_6H_4\begin{cases}CH_2COOH\\CN\end{cases}$ becomes $C_6H_4\begin{cases}CH_2—CO\\CO—NH\end{cases}$,

but $C_6H_4\begin{cases}CH_2.CN\\COOH\end{cases}$ does not rearrange.

Diphenic Acid and Acetonitril.—Diphenic acid and acetonitril in equal molecular proportions were heated together in a sealed tube for six hours, the temperatures increasing gradually from 225° to 240° C. A strong odor of acetic acid was noticed when the tube was opened. The contents were treated with cold dilute sodium carbonate solution and the solid crystalline residue was thrown upon a filter and washed with water. This product was dissolved in warm chloroform and from this solution long needles melting at 217° C. (uncorrected) were obtained. These crystals may be sublimed and were proved to be diphenimid by tests to be mentioned later. Recrystallized and treated with boneblack, long, colorless crystals, melting at 217.5° C., were obtained from alcoholic solution. There has been a difference of opinion among chemists as to the melting-point of diphenimid and diphenamid, respectively. Wegerhoff states that the imid and amid both melt at 215°. Graebe and Aubin give the melting-point of the imid as 219°–220° and of the amid as 208°–209°.[1] Later Wegerhoff[2] gives figures differing from his own statement in the *Berichte*, **21**, 2356; *viz.*, 212°–213° and 217° for the amid and imid respectively. There is an obvious reason for different results upon the amid because it decomposes readily, losing ammonia, and gives the imid. My own experience confirms Wegerhoff's figures last mentioned. In determining the melting-point of diphenamid different results were obtained depending upon the rapidity with which it is heated to the point of fusion. By slow heating decomposition is gradual; the melting-point tube becomes clouded and complete fusion may not take place before 217°, while by rapid heating no apparent decomposition takes place and the crystals melt at 212°–213° C.

To confirm my results, I tested the diphenimid as follows: By standing with cold, concentrated ammonia, hexagonal crys-

[1] *Ann. Chem.* (Liebig), **247**, 270.
Ibid. **252**, 16.

tals separate out. These melt at 212°–213°, give off ammonia by heating, and are apparently diphenamid. The separation of the crystals takes place almost immediately if the ammonia solution is warmed. By boiling diphenimid with concentrated potassium hydroxide solution, ammonia is evolved. The first product of the action of potassium hydroxide, however, is this :

$$\begin{matrix} C_6H_4.CO \\ | \\ C_6H_4.CO \end{matrix} > NH + KOH = \begin{matrix} C_6H_4.CONH_2 \\ | \\ C_6H_4.COOK \end{matrix}.$$

By acidifying with hydrochloric acid and cooling after the brief action of potassium hydroxide solution, colorless plate-like crystals of diphenamic acid were deposited, melting at 190°–191° C. Diphenimid is almost entirely insoluble in boiling water. The yield of diphenimid by the reaction tried was about ninety per cent. of the theoretical, estimated upon the product once crystallized from chloroform. The reaction which accounts for this production of diphenimid is :

$$\begin{matrix} C_6H_4.COOH \\ | \\ C_6H_4.COOH \end{matrix} + CH_3CN = \begin{matrix} C_6H_4.CO \\ | \\ C_6H_4.CO \end{matrix} > NH + CH_3.COOH.$$

o-Sulphobenzoic Acid and Acetonitril.—The *o*-sulphobenzoic acid used in this series of experiments was made by Remsen's method from saccharin.[1] Briefly, the method is to decompose saccharin by boiling with strong hydrochloric acid. This solution is evaporated to dryness and cold water added. This dissolves the acid ammonium salt of *o*-sulphobenzoic acid, $C_6H_4\begin{matrix} COOH \\ SO_2NH_4 \end{matrix}$, which is the first product of the decomposition of saccharin with hydrochloric acid. Any *p*-sulphaminebenzoic acid which the saccharin may have contained remains undissolved. The water solution, by evaporation and cooling, gives large diamond-shaped crystals of the ammonium salt. These are treated with phosphorus pentachloride. The mixture becomes semi-fluid, owing to the production of oxychloride of phosphorus and sulphobenzodichloride,

[1] *Am. Chem. J.*, II, 332.

The reaction-product is poured in ice-water and a yellow oily layer of the acid chlorides separates and is thoroughly washed and then decomposed by boiling with water, producing *o*-sulphobenzoic acid. This crystallizes from a concentrated aqueous solution with four molecules of water of crystallization. To obtain the anhydrous acid, it was heated at 130°–135° several times, alternately cooling it in a vacuum desiccator over sulphuric acid. The last traces of water are hard to remove and at a temperature a little above that necessary to keep the sulphobenzoic acid liquid, it begins to darken.

An error seems to have crept into the literature of this compound regarding its melting-point. It is stated in nearly all the chemistries that have been consulted that *o*-sulphobenzoic acid melts at 250°. The melting-point is 68° for the hydrated acid and about 130° for the anhydrous. The acid ammonium salt mentioned above melts between 250°–260°, and this compound, when first made and described, was thought to be the free acid.[2]

The sulphobenzoic acid thus prepared was heated with acetonitril in equal molecules at 165°–170° for five hours. The first set of tubes examined exhibited no pressure upon unsealing and showed a light brown sirupy material in which were seen transparent crystals. The tube contents were treated with cold, absolute alcohol. The sirupy part dissolved readily and the crystals remained. They were soluble in hot absolute alcohol and were crystallized from this medium. They then appeared as large, diamond-shaped plates, melting at about 260°. They gave a nitrogen test and were acid in reaction and taste. They seemed to be the acid ammonium salt of sulphobenzoic acid, and their presence is explained by the fact that the first sulphobenzoic acid prepared was not completely anhydrous. A portion of it, further heated at 135° and then treated with the nitril as before, gave only the sirupy material. The second lot of sulphobenzoic acid prepared gave, when heated with the nitril, no residue insoluble in cold absolute alcohol. Some of the dia-

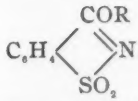
[1] Remsen: *Ibid*, 17, 309.
[2] Brackett, Hayes: *Ibid*, 9, 405.

mond-shaped crystals were boiled with potassium hydroxide and evaporated to dryness. The residue, by treatment with phosphorus pentachloride, gave a yellow oily substance resembling *o*-benzosulphodichloride. This disappeared by adding ammonia, probably with the formation of an amid.

The sirupy portion in alcohol solution, treated with boneblack and evaporated to dryness, became crystalline by cooling. When redissolved in alcohol and set aside to crystallize, minute, indistinct, white crystals separated. They give a faint acid reaction to litmus and phenolphthalein, no reaction with methyl orange. They contain nitrogen and sulphur, are very soluble in water and alcohol, insoluble in ether. They do not form an ammonium salt by evaporating to dryness with ammonia water and seem to be unchanged by this treatment. They possess no sweet taste. The first product of this kind examined melted at 220°–221°. This is the same melting-point as that given for saccharin. The product from the second set of experiments melts at 225°. I have reason to believe that this was a purer product than the first material examined. It softens before melting and the melting-point tube becomes clouded. It is not sweet after melting and begins to darken a little above its melting-point.

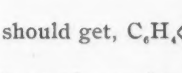
From the parallel with phthalic acid it was expected that these experiments might give saccharin, $C_6H_4\begin{cases}CO\\ >NH\\ SO_2\end{cases}$, or possibly its isomer *o*-sulphobenzonitril, $C_6H_4\begin{cases}CN\\ SO_2H\end{cases}$. The product is not the latter compound because its solution does not decompose carbonates and an ammonium salt corresponding to that described by Remsen[1] could not be formed. Its different solubilities and lack of sweet taste show that it is not saccharin, but a quantitative determination of nitrogen shows it to be isomeric with it, and it may therefore be the unsymmetrical sulphobenzimid, $C_6H_4\begin{cases}CNH\\ >O\\ SO_2\end{cases}$. Still another isomer is possible, pseudosaccharine, whose derivatives of this type are known,

[1] *Am. Chem. J.*, 18, 819.



More thorough investigation will be made of our compound to establish its constitution. The determination of nitrogen resulted as follows:

	1.	2.
Weight of sample	0.3187	0.3333
Weight of nitrogen	0.0232	0.0252
Per cent. nitrogen	7.28	7.56
" " calculated for $C_7H_5O_3SN$.	7.65	

The presence of the acid ammonium salt of sulphobenzoic acid in our first tubes is really a confirmation of the fact that the main reaction has given an imid, for by the action of water we should get, 

, just as is the case when saccharin is acted upon by strong hydrochloric acid, whereas if *o*-sulphobenzonitril had been formed, it would have given *o*-sulphobenzamid by the action of water under pressure.

Mellitic Acid and Acetonitril.—A tube containing mellitic acid (one molecule) and acetonitril (three molecules) with a few drops of acetic anhydride, was heated four hours at 265°–275° C. The contents of the tube were very dark-colored and were extracted with water and washed on the filter until the washings were no longer acid. The insoluble residue being still dark was extracted with alcohol and with dilute sodium carbonate solution. Very little material dissolved by this treatment, but this residue was lighter colored. Nitrogen was tested for in this residue and its presence detected.

The sodium carbonate washings, by acidifying, gave a very dark and mostly flocculent precipitate. This gave the euchronic acid test. The final residue, after the extraction mentioned above, was insoluble in hydrochloric acid, but dissolved in sulphuric. When the acid solution was poured into water and let stand a very fine precipitate appeared. This was paramid and still retained its brown tint.

This experiment was repeated at a lower temperature, heating for three hours at 180°–200°, and three hours at 225°–235° C. The tube contents were only slightly discolored. About

ninety per cent. of the paramid was found after extractions with hot water and with very dilute ammonia had been made. The insoluble residue dissolves in strong ammonia and gives a precipitate which seems to be euchronamic acid upon the addition of hydrochloric acid. This precipitate, as was stated by Wöhler, yields the same color reactions as euchronic acid.

The color imparted to a solution by euchron is very unstable. It disappears instantly by shaking with access of air and in a test-tube containing a solution of a very small amount of euchronic acid a color may appear at the bottom when the zinc is added while the top of the solution remains colorless. The purple-red color obtained in an alkaline solution behaves in the same way, but is a more delicate test for the presence of euchronic acid. The red color is produced whether the zinc is added first to the water solution and then ammonia added, or the zinc may be added to an ammoniacal solution of euchronic or euchronamic acid. If paramid and zinc dust be shaken together in water, no color reaction takes place, but by adding ammonia a red color appears, showing the production of euchronamic acid.

Schwartz[1] found very few reducing agents available for producing euchron. In the course of this investigation it was discovered that aluminum amalgam gives the red color. The reaction progresses slowly, the aluminum foil being first colored red, before any color is imparted to the solution.

In the examination of the contents of tube II it was found that the original water extraction, upon cooling, gave a crystalline precipitate. This was filtered off and found to be readily soluble in hot water, from which it could be precipitated by adding nitric acid. The crystals thus obtained were square prisms of euchronic acid. In working with mixtures containing euchronic acid one notices that nearly every solution obtained during the examination will give euchron by adding zinc dust, provided the solution tested is not strongly acid with inorganic acid. The color reaction in alkaline solution is so delicate that one part of euchronic acid in more than 100,000 parts of solvent may be detected. Under such conditions the

[1] *Ann. Chem.* (Liebig). 66, 46.

color develops slowly and the solution should be kept corked during the test.

It was thought by heating together equal molecules of mellitic acid and acetonitril that mellitmonimid would result. A tube containing these reagents and a few drops of acetic anhydride were heated during four and one-half hours at 215°–220°. The tube contents were white and all soluble in water. No monimid was found, only euchronic acid and unchanged mellitic acid being produced. A repetition of this experiment verified these results, a large amount of euchronic acid having been found. Euchronic acid crystallizes from water in the form of six-sided plates and in long prisms from an acid solution.

Another attempt to prepare mellitmonimid was made by employing the two-thirds neutralized mellitic acid. A standard solution of sodium hydroxide was used and four of the six carboxyls were saturated. The solution was evaporated to dryness and dehydrated. The acid salt remaining was heated with acetonitril for several hours at 230°, and even at 290° no nitrogen was found to have entered the mellitic compound. This argues rather that the sodium atoms have not entered consecutively than that there is any reason why a monimid should not exist.

The conversion of paramid into euchronamic acid would indicate that Wöhler's euchronic acid is an ortho compound. In confirmation of this the following experiment should be recorded. A quantity of euchronic acid was dried at 200°. The crystals do not lose their form at this temperature but become opaque and dull. The dried euchronic acid was heated with an excess of acetonitril for three and a half hours at 223° C. Paramid was not produced and the euchronic acid was recovered and tested. As the paramid of my previous experiments had been made at a higher temperature than 223°, the experiment was repeated at 240°–260° C. After three hours' heating the contents were examined and paramid found. The reaction was not complete, for some euchronic acid was recovered. This seems to show that the carboxyls of this euchronic acid are in the ortho position. The paramid produced in these experiments was always dark-colored and no means of purification has been found. The euchronic acid, however, was always white or a very pale yel-

low tint. The reactions which have been found to take place in this series of experiments are :

1. $C_6(COOH)_6 + 3CH_3CN = C_6(C_2O_2NH)_3 + 3CH_3.COOH.$
2. $C_6(COOH)_6 + 2CH_3.CN = C_6(C_2O_2NH)_2(COOH)_2 + 2CH_3COOH.$
3. $C_6(C_2O_2NH)_2(COOH)_2 + CH_3.CN = C_6(C_2O_2NH)_3 + CH_3COOH.$

Another series of experiments was tried upon the partly neutralized mellitic acid, two objects being in view ; *i. e.*, the determination of the order in which the carboxyls combine with sodium, and second, to prepare the other two possible imids. Only partial success was obtained along both these lines. If large quantities of mellitic acid could be used, so that the partially neutralized salts could be isolated and crystallized, there is no doubt that both of these objects would be attained. Two tubes containing the tetra acid disodium salt [$C_6(COO)_6H_4Na_2$] were heated with acetonitril, two molecules of the latter to each molecule of the acid salt. They received five hours' heating at 225°–240°. Very slight pressure was noted upon opening. The contents were washed with ether several times and with ninety-five per cent. alcohol. The ether extract contained acetic acid. The solid contents were soluble in water and by acidifying thin needle-like crystals came down. Recrystallized from water they came down as thin plates. These crystals give the euchron test but are very different from the euchronic acid previously prepared. They consist of large thin plates, imperfectly formed and twinning somewhat. They give an acid reaction and do not melt below 295° C., but lose water of crystallization. They undergo no other change at this temperature and after heating give the euchron test as before. To further prove that they were not *o*-euchronic acid they were heated for five hours at 240°–260° with propionitril. No paramid was produced. The *p*-euchronic acid recovered was recrystallized from water and gave very thin six-sided plates. The first two sodium atoms seem to have entered at 1 and 4. From two tubes, in, which what was thought to be the triacid trisodium salt had been used and heated with nitril as before, no monimid was isolated. It may be that the saturation with sodium hydroxide gives a mix-

ture of compounds, for euchronic acid was obtained from this experiment. Its analysis resulted as follows:

	H_2O. Per cent.	N. Per cent.
$C_{12}O_8H_4N_2(+ 2H_2O)$	10.6	9.31
Found	10.0	9.13

The figures for nitrogen are based upon the anhydrous euchronic acid. The previous experiments upon the tetrasodium salt of mellitic acid show that the sodium atoms enter at 1, 2, 4, and 5.

CONCLUSIONS.

In the foregoing experiments it has been shown that

I. Cyanacetic acid under certain conditions appears to rearrange to yield its isomer malonimid.

II. Benzoic acid and ethylene cyanide give benzonitril and succinimid.

III. Phenylacetic acid and ethylene cyanide give phenylacetonitril and succinimid. As a secondary product phenylacetic acid and phenylacetonitril give diphenyldiacetamid.

IV. In II and III it seems probable that β-cyanpropionic acid is an intermediate product and rearranges to give succinimid, and that in general, when an imid is produced by this reaction, it may be considered as resulting from an intermediate cyanacid.

V. The substituted monobasic acids, salicylic and anthranilic, give no similar results on account of the decompositions they undergo by heating.

VI. Phthalimid results from phthalic acid and propionitril, and phthalimid and succinimid result from phthalic acid and ethylene cyanide.

VII. Phthalic anhydride and acetonitril do not react under the conditions presented.

VIII. Terephthalic acid and propionitril do not react under the conditions presented.

IX. Homophthalimid is not readily formed from homophthalic acid and a nitril. It does not result by a rearrangement of cyan-*o*-toluic acid.

X. Diphenimid results in nearly theoretical amounts from diphenic acid and acetonitril.

XI. *o*-Sulphobenzoic acid and acetonitril yield a compound isomeric with saccharin which may be the unsymmetrical *o*-sulphobenzimid.

XII. By varying the conditions three of the four possible imids of mellitic acid were produced by heating this acid with acetonitril. The *p*-euchronic acid is a new compound; *o*-euchronic acid and paramid were known but have resulted also by our nitril reaction. It has been shown that aluminum amalgam can be used to give the euchron test.

To sum up then briefly, I believe I have made three new imids; *viz.*, malonimid, *p*-euchronic acid, and an imid of sulphobenzoic acid. The known imids of succinic, phthalic, homophthalic, diphenic, and mellitic acids have been made by a new method. The conclusions of Colby and Dodge, stated in the introduction, have been confirmed and the first method used by Miller and Seldner for producing fatty imids has been found applicable for producing aromatic imids. The widest general conclusion to be drawn from the work of these earlier investigators of the action of nitrils upon acids and from my own work is that when acids and nitrils are heated together they tend to form disubstituted ammonia compounds, secondary amids from monobasic acids and nitrils, imids from dibasic acids and nitrils.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 2.]

THE ACTION OF METALLIC THIOCYANATES UPON ALIPHATIC CHLORHYDRINS.[1]

BY WILBER DWIGHT ENGLE.

Received July 7, 1898.

THE alcohols form the most important class of organic compounds which have no representatives containing the thiocyan group. It would seem that such compounds would be produced by the double decomposition between alcohols having one or more atoms of hydrogen displaced by halogen and a metallic thiocyanate, and it was with this expectation that the following experiments were undertaken. In all cases tried, a reaction occurred as was shown by the separation of the halogen

[1] Read at the meeting of the New York Section, May 6, 1898.

salt. The thiocyanates formed, however, seem to be very unstable, easily changing to resinous substances, and much difficulty was experienced in separating and purifying them. In some cases it was found impossible.

The particular thiocyan alcohols, whose preparation was undertaken, are those derived from propane; namely, α-thiocyanhydrin, $\begin{matrix}CH_2SCN\\|\\CHOH\\|\\CH_2OH\end{matrix}$, α,β-dithiocyanhydrin, $\begin{matrix}CH_2SCN\\|\\CHSCN\\|\\CH_2OH\end{matrix}$, and α,γ-dithiocyanhydrin, $\begin{matrix}CH_2SCN\\|\\CHOH\\|\\CH_2SCN\end{matrix}$. As being of a somewhat similar nature, the epithiocyanhydrin, $\begin{matrix}CH_2SCN\\|\\CH\\|\\CH_2\end{matrix}\!\!>\!O$, the α-acetodithiocyanhydrin, $\begin{matrix}CH_2SCN\\|\\CHSCN\\|\\CH_2OOC_2H_3\end{matrix}$, and β-acetodithiocyanhydrin, $\begin{matrix}CH_2SCN\\|\\CHOOC_2H_3\\|\\CH_2SCN\end{matrix}$, were prepared.

α-THIOCYANHYDRIN.

For the attempted preparation of α-thiocyanhydrin the corresponding α-chlorpropylene glycol or monochlorhydrin, $\begin{matrix}CH_2Cl\\|\\CHOH\\|\\CH_2OH\end{matrix}$, was used.

A mixture of fourteen grams of monochlorhydrin and thirteen grams of potassium thiocyanate, with ninety-five per cent. alcohol for solution, were heated on the water-bath with a return condenser. A crystalline precipitate of potassium chloride gradually formed. After four days of heating, four grams of potassium chloride in place of ten grams, theoretical quantity,

had separated. The filtrate from the potassium chloride was again heated. Only a little more of the chloride separated but there formed a considerable amount of a white resinous substance, some of which was removed from the flask and examined. Washed with hot water and alcohol it is a white or light yellow, brittle, odorless substance. It is insoluble in ordinary organic solvents, including water, alcohol, ether, benzene, chloroform, carbon disulphide, benzine, kerosene, gasolene, and toluene. It is unaffected by hydrochloric, acetic, and sulphuric acids or by ammonium hydroxide or strong aqueous potassium hydroxide. Bromine decomposes it with the production of a tar-like substance. Strong nitric acid oxidizes it, producing sulphuric and oxalic acids. This is an interesting reaction since it shows that the sulphur is much less closely bound to the radical than in the case of thiocyanates, mercaptans, and sulphides which, by oxidation with nitric acid, yield sulphonic acid, sulphoxids, and similar compounds.

That this resinous substance is not a thiocyanate is shown by the following facts: It does not give a sulphide with potassium hydroxide. It does not give a mercaptan with zinc and sulphuric acid. It does not give a sulphide and potassium thiocyanate with potassium sulphide. It does not give a sulphonic acid by the oxidation with nitric acid. Its solubilities are not those of known thiocyanates.

An analysis of the substance carefully washed with water and alcohol and dried to a constant weight, gave the following percentages, from which it is impossible to calculate any simple formula:

	I.	II.	III.	IV.	V.	Average.
Carbon	40.127	40.163	....	....	....	40.145
Hydrogen	5.185	5.15	....	....	....	5.168
Nitrogen	....	....	7.531	7.590	....	7.560
Sulphur	....	....	....	....	27.281	27.281
Oxygen	....	....	....	....	....	19.846

These percentages indicate that a secondary reaction has produced a complex condensation product. The absence of any solvent prevented any attempt to crystallize this compound. A flask, containing a mixture of potassium thiocyanate and monochlorhydrin, after heating was set aside. After several weeks it

was examined and well-formed crystals were found. The properties of these crystals were identical with those of the substance just described.

Besides the insoluble white substance there was also found, in the alcoholic filtrate from the potassium thiocyanate and monochlorhydrin, a very small amount of oil having the garlic odor characteristic of the organic thiocyanates. This oily liquid is extremely unstable. Any attempt to purify it changes it to the insoluble white substance. Apparently the monothiocyanate is first formed by the reaction, and by some secondary condensation the insoluble compound results.

The reaction between potassium thiocyanate and monochlorhydrin was also tried at higher temperatures. Sealed tubes containing these two compounds in the ratio of their molecular weights, with alcohol as a solvent, were heated to different temperatures. Below 100° the action was very slow. From 110° to 115° the reaction was complete in six hours. At 120° and above there was much decomposition. In all cases the products are the same: the insoluble white compound and a trace of what was considered the monothiocyanhydrin. It was impossible to secure this in amount sufficient for further study.

α,β-DITHIOCYANHYDRIN.

The α,β-dibromhydrin, $\begin{matrix} CH_2Br \\ | \\ CHBr \\ | \\ CH_2OH \end{matrix}$, to be used in the preparation of α,β-dithiocyanhydrin, was obtained by the direct addition of bromine to allyl alcohol,

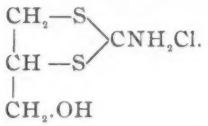
$$C_3H_5OH + 2Br = C_3H_5Br_2OH.$$

The product was purified by distillation *in vacuo*.

An alcoholic solution of forty grams of this dibromhydrin and thirty-seven grams of potassium thiocyanate were heated on the water-bath for six days. Somewhat more than half the theoretical quantity of potassium bromide separated. As there were signs of decomposition the heating was stopped. By evaporation of the alcohol, washing with water, and collecting with ether, about ten cc. of a dark-colored liquid was obtained.

Heated with potassium sulphide solution it gave potassium thiocyanate easily identified by the ferric chloride test. On heating or attempting to distil with steam it was resinified.

The reaction was next tried in sealed tubes. The tubes were charged with potassium thiocyanate and dibromhydrin, in the ratio of two molecules of the former to one of the latter. Alcohol was added as a solvent. Between 110° and 115° the reaction was complete in about eight hours. At higher temperatures there was much decomposition. In all cases there was a tendency to produce an amorphous substance similar to that from the monochlorhydrin. The contents of the tube were treated with warm alcohol. The alcoholic solution filtered from the potassium bromide was slowly evaporated to a small bulk and carefully washed with water to remove any unchanged potassium thiocyanate. There was left an oily liquid which could be further purified by solution in ether. This treatment does not remove all the unchanged dibromhydrin. The compound decomposes on heating, hence cannot be distilled. The difficulty of securing a pure sample prevented analysis. That the liquid is dithiocyanhydrin is shown by the fact that it gives potassium thiocyanate on heating with potassium sulphide, and the yield of potassium bromide is nearly equal to the theoretical. Additional proof is found in the preparation from it of iminomethanepropylalcohol disulphide hydrochloride of the formula



A similar reaction is found in the case of methylene dithiocyanate and propylene dithiocyanate. Both compounds have adjacent thiocyan groups as in the case of the compound under discussion and both give imino compounds similar to that above.[1]

About ten cc. of dithiocyanhydrin was poured into fifty cc. of water and a few grams of granulated tin added. The mixture was carefully heated on the water-bath and hydrochloric acid added. In the course of an hour's boiling the oily dithiocyan-

[1] Hagelberg: *Ber. d. chem. Ges.*, **23**, 1083.

hydrin disappeared. Upon evaporation to a small bulk crystals appeared. When the liquid was left to spontaneous evaporation large octahedrons were obtained of iminomethanepropylalcohol disulphide tin hydrochloride.

The compound is not stable in solution as the tin (stannous) is oxidized at the expense of the rest of the compound producing stannic chloride and a resinous substance. It was found advisable to precipitate the tin immediately after the dithiocyanhydrin had gone into solution, with hydrosulphuric acid, leaving the hydrochloric salt of iminomethanepropylalcohol disulphide in solution. The solution, filtered from the tin sulphide, was evaporated to dryness on the water-bath. The residue was dissolved in alcohol, filtered, evaporated to a small bulk, and allowed to crystallize. Transparent, colorless, well-formed, tetragonal crystals separated. A determination of the chlorine gave 20.21 per cent., while the formula

$$\begin{matrix} CH_2—S \\ CH—S \\ CH_2OH \end{matrix} > C : NHHCl,$$

requires 20.08 per cent.

This iminomethanepropylalcohol disulphide hydrochloride is very easily soluble in water, somewhat soluble in alcohol, and insoluble in ether and chloroform.

The preparation of this compound taken with the reactions with potassium sulphide and the amount of potassium bromide separated, identify the dithiocyanhydrin. The reaction for its preparation is

$$C_3H_5OHBr_2 + 2KSCN = C_3H_5OH(SCN)_2 + 2KBr.$$

In its physical properties it closely resembles the propylene-dithiocyanate. Both are liquids of garlic-like odor, insoluble in water, but soluble in alcohol and ether. Both are decomposed by heat and resinified by acids and alkalies. By nitric acid both are oxidized, producing sulphuric acid and, in the case of dithiocyanhydrin, oxalic acid is also formed. The action of the nitric acid seems to be to first produce a substance similar to the amorphous compound from the monochlorhydrin which is then oxidized as above.

α-ACETODITHIOCYANHYDRIN.

Acetodibromhydrin, or dibrompropyl acetate, is prepared by the action of acetic anhydride on the α,β-dibrompropyl alcohol.[1] It was washed with water and a dilute carbonate solution, dried and rectified under diminished pressure.

A sealed tube containing seventeen grams of acetodibromhydrin, thirteen grams of potassium thiocyanate, and ten cc. of alcohol, was kept at 120° for four hours. On opening, nearly the theoretical quantity of potassium bromide was found. The alcoholic filtrate from the potassium bromide was poured into water and about fifteen cc. of a heavy liquid, insoluble in the water, separated. This was washed several times with water to free it from traces of potassium bromide and thiocyanate. It was then dissolved in ether to free it from decomposition-products. On evaporation there was left a clear, red-colored liquid, giving with potassium sulphide, potassium thiocyanate. This compound, like the corresponding alcohol, cannot be distilled and is easily decomposed by most reagents. With tin and hydrochloric acid it gave reactions similar to those with the alcohol.

The compound was not analyzed but the reactions show it to be acetodithiocyanhydrin. The reaction is:

$$C_3H_5.Br_2OOC_2H_3 + 2KSCN = C_3H_5(SCN)_2OOC_2H_3 + 2KBr.$$

α,γ-DITHIOCYANHYDRIN.

The dichlorisopropyl alcohol or dichlorhydrin was prepared by treating anhydrous glycerine with chloride of sulphur at 100°. The product was fractionally distilled and the fraction collected between 176° and 178° was used in these experiments.

A mixture of twelve and five-tenths grams of the dichlorhydrin and nineteen grams of potassium thiocyanate in alcoholic solution was heated on the water-bath for four days. About six grams of potassium chloride had separated, less than half the theoretical amount. The contents of the flask had the odor of the thiocyanates. In addition to the potassium chloride there had also separated a spongy mass, of a yellow color, and in appearance not unlike the insoluble compound obtained from the monochlorhydrin. On examination it showed the same properties. It was insoluble in the organic solvents. It was unaffected by acids or alka-

[1] Aschan: *Ber. d. chem. Ges.*, **23**, 1827.

lies. Reducing agents do not change it; strong nitric acid oxidizes it to sulphuric and oxalic acids. It is apparently a condensation-product similar to that obtained in case of monochlorhydrin.

In the alcoholic filtrate from the above compound was found a very small amount of a liquid, insoluble in water, having the characteristic odor of the thiocyanates. It may have been either the dithiocyanhydrin sought or the chlorthiocyanhydrin. Its insolubility in water would distinguish it from the dichlorhydrin. It was unstable and attempts to purify it sufficiently to test resulted in its decomposition.

This reaction was also tried in sealed tubes. A tube, heated to 130° for six hours, contained much unchanged potassium thiocyanate. Considerable of the spongy substance was found and a trace of the oily compound mentioned above. A tube heated to 175° for two hours gave the best results. The action was nearly complete. Less of the amorphous substance was formed. At higher temperatures there was much decomposition and pressure produced. In all cases the same results were obtained. I was unable to separate and purify a compound containing the thiocyan group.

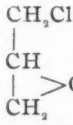
β-ACETO-α,γ-DITHIOCYANHYDRIN.

The corresponding acetic ester, the dichlorisopropylacetate, was also tried. The ester was prepared according to the method of Berthelot and Luca.[1] Anhydrous glycerine was treated with acetyl chloride and the product purified by fractional distillation.

A sealed tube containing dichlorpropyl acetate and potassium thiocyanate in the ratio of one molecule of the former to two of the latter, with alcohol for solution, was heated to 130° for six hours. The action was incomplete and the tube was heated to 180°. There was some decomposition. A large amount of amorphous substance resembling those already described was present. A small amount of oil was also found as in the case of the corresponding alcohol. Here, again, apparently the thiocyanate is formed but suffers secondary decomposition resulting in the insoluble amorphous substance.

[1] *Ann. chim. phys.* [3], **52**, 459.

EPITHIOCYANHYDRIN.

Epithiocyanhydrin proved much easier in preparation and more interesting in reactions. For its preparation both epichlorhydrin,  , and epibromhydrin were used. Epichlorhydrin was obtained by the action of a strong aqueous solution of potassium hydroxide on dichlorisopropyl alcohol. The epibromhydrin was obtained in a similar manner from α,β-dibrompropyl alcohol. Both compounds were purified by distillation.

There is no reaction between epibrom- or epichlorhydrin and potassium thiocyanate at ordinary temperatures. Mixtures of these substances have stood for several days without reaction. At 40° to 50°, however, the action goes on nicely. The theoretical amount of potassium halogen salt is separated in a few hours. At higher temperatures the action is violent; at 100° it is very rapid and there is much decomposition. The purification of the epithiocyanate is somewhat difficult as heat decomposes it. The alcoholic solution, filtered from the separated potassium chloride or bromide is evaporated to a small bulk, keeping the temperature below 50°. Water is then added to wash out the excess of potassium thiocyanate. A thick insoluble liquid separates; this is the epithiocyanhydrin holding in solution much decomposition matter. It can be freed from this, after washing with water, by solution in ether. The evaporation of the ether leaves the epithiocyanhydrin as a clear liquid of a dark red color, and having a disagreeable garlic odor. It is insoluble in water but soluble in alcohol, ether, and chloroform. It cannot be distilled. On the skin it produces a burning or smarting sensation. With potassium sulphide it gives potassium thiocyanate. With nitric acid it behaves like the compounds already described: the acid first resinifies and then oxidizes to sulphuric and oxalic acids.

A determination of the nitrogen confirms the qualitative results:

	Per cent.
Nitrogen found	11.914
Necessary for formula, $\begin{matrix}CH_2SCN\\CH\\CH_2\end{matrix}>O$	12.17

The reaction is:

$$C_3H_5O.Cl + KSCN = C_3H_5O.SCN + KCl.$$

ACTION OF HYDROSULPHURIC ACID ON EPITHIOCYANHYDRIN.

Dry hydrosulphuric acid has an interesting reaction on the thiocyanates of the marsh-gas series. It forms the esters of dithiocarbamic acid which are readily crystallizable. About ten cc. of epithiocyanhydrin was treated with hydrogen sulphide under a pressure of one atmosphere and eight inches of mercury. The experiment was tried both at ordinary temperatures and at 100°. In both cases the result was the same. No carbamic ester was formed, but thick sirupy liquid of a very disagreeable odor, insoluble in water and sparingly soluble in alcohol, carbon disulphide, and chloroform. Its alcoholic solution was precipitated by soluble lead, mercury, silver, and copper salts, but was unaffected by mercuric or lead oxids. These reactions indicate the formation of a sulphide.

EPIHYDRINDIMETHYLSULPHIN IODIDE.

A reaction similar to that used by Cahours in the preparation of trimethylsulphin iodide was tried. About five cc. of epithiocyanhydrin with fifteen cc. of methyl iodide (an excess) were sealed in a tube and kept at 100° for six hours. On examination crystals were found in the tube. A similar mixture was allowed to stand for several days at the ordinary temperature, and crystals also separated in this case. The crystals were clear, colorless, monoclinic plates. They were purified by recrystallizing from water and washing with alcohol. They gave good qualitative tests for both sulphur and iodine. The iodine was determined both by titration, with a standard silver nitrate solution, and by weighing the precipitated silver iodide:

	Per cent.
Iodine found	51.392
Necessary for the formula, $\begin{matrix}CH_2(CH_3)_2SI\\CH\\CH_2\end{matrix}>O$	51.430

The crystals decompose without melting between 195° to 200°.

The small amount of material prevented farther experiments.

The compounds most closely related to epithiocyanhydrin are the thiocyanacetone and thiocyanpropyl aldehyde. It resembles both in physical properties and in its unstable character.

The thiocyanacetone was reported by Tscherniac in 1883. It is an oil of very disagreeable odor and easily decomposed by heat.

The β-thiocyanpropyl aldehyde was prepared by Chautard.[2] It is a liquid of fetid odor, is decomposed by heat, and is easily resinified by acids and alkalies.

CONCLUSION.

The results of the experiments may be summarized as follows:

The monochlorhydrin, the α,γ-dichlorhydrin, and the acetodichlorhydrin, form corresponding thiocyanates which are very unstable and immediately change to complex secondary compounds.

The α,β-dibromhydrin and its acetic ester form dithiocyanates which are somewhat more stable and can be separated and purified. Treated with tin and hydrochloric acid they give double chlorides of tin and iminomethanepropylalcohol disulphide.

The epichlorhydrin forms the epithiocyanhydrin readily. It is a liquid of garlic odor, insoluble in water, but soluble in alcohol and ether. It cannot be distilled. With dry hydrosulphuric acid it forms epihydrin sulphide rather than a dithiocarbamic ester. With methyl iodide it forms epihydrindimethylsulphine iodide.

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LUBRICANTS FOR GLASS STOP-COCKS.

BY FRANCIS C. PHILLIPS.

Received July 18, 1898.

THE success of modern chemical research work depends frequently upon the maintenance in position for considerable periods of complex forms of apparatus in which glass stop-

[1] Tschmerniac: *Ber. d. chem. Ges.*, **16**, 349.

[2] Chautard: *Ann. chim. phys.* [6], **16**, 197.

cocks play an important part, and the failure or breakage of a stop-cock often proves to be the cause of serious loss of time or material. The efficiency of a stop-cock is, however, quite as much dependent upon the lubricant used for its protection as upon the skilful workmanship of the glass-blower in its manufacture.

It has been the common practice to employ an animal fat or a mixture of such fats for lubricating the stop-cock plugs of apparatus of all kinds and for work of every description, although it is a fact of experience that such lubricants are often a source of inconvenience and even danger to the apparatus.

A stop-cock lubricant should, besides overcoming friction, satisfy the following requirements:

1. It should adhere to the glass and should not be loosened by water.

2. It should be little affected by changes of temperature.

3. It should not be saponified by alkali.

4. It should be sufficiently transparent or translucent to render visible any clogging of the hole in the stop-cock plug while in use, and to show whether air spaces occur between the plug and the walls of the stop-cock.

Ordinary fats are so easily saponified and adhere so feebly to glass that they are seldom suited to the purpose. Pure rubber heated to a temperature sufficient to render it permanently viscid, has advantages over fats, but its adhesiveness is lessened by moisture, and it is completely removed by alkali.

Schmitz[1] recommends for glass stop-cocks the use of gutta percha dissolved in a high-boiling mineral oil. This mixture, although not saponifiable, does not adhere well to glass. If thinned down sufficiently with oil, its lubricating qualities suffer, while the gutta percha tends to become granular if the mixture is made thicker.

Vaseline, which is sometimes recommended for use alone, does not adhere to the glass, and does not overcome friction.

With a view to producing a lubricant better adapted to use on glass stop-cocks, a series of experiments has been tried. Various mixtures of softened rubber with other substances were tested. On mixing together

[1] *Ztschr. anal. Chem.*, *1884*, 516.

	Parts.
Pure rubber	70
Spermaceti	25
Vaseline	5

a mass is obtained which lubricates well, is translucent, adheres to the glass, and is not saponifiable. The vaseline was added to the mixture to increase its softness. The materials were thoroughly mixed while hot, the rubber being melted first, and the others stirred in. It is well to use a little more vaseline in winter than summer.

Another preparation, which gave still better results, was made by mixing

	Parts.
Pure rubber	70
Yellow unbleached beeswax	30

The rubber should be pure and fresh. Old rubber, or scraps of worn-out tubing, whether black or red, will not answer as well and may cause the mixture to become more or less granular and opaque when used in the stop-cocks. The rubber is best heated in a covered vessel until thoroughly melted, and then the wax should be added. The hot mixture is well stirred. No vaseline is needed. This lubricant is very serviceable, protects stop-cocks from sticking, even when used for concentrated solutions of caustic alkalies, and is quite translucent in thin layers. Care should be used not to scorch the mixture in its preparation. Strong alkalies tend in time to loosen and emulsify all lubricants and the stop-cocks should occasionally be cleaned and recoated.

It has been attempted to increase the adhesiveness of such lubricants by the addition of small quantities of balsam of fir and other strongly adhesive substances, but difficulty was found from the tendency to cause sticking of the stop-cock plug. The rubber mixtures should not be exposed to the air longer than is necessary during the heating, and they should be preserved in closed bottles.

Various mixtures of gutta percha with wax and with oils were tried but the gutta percha tends to cause granulation and diminishes adhesiveness. The mixtures above recommended may be readily removed from parts of glass apparatus which are difficult of access for cleaning, by the use of a little concentrated

nitric acid, which quickly attacks and loosens it so that it may be washed out by water.

No lubricant is fit for use unless it renders the stop-cock nearly or quite translucent, so as to show whether or not the plug is coated over its entire length.

A thick rubber and wax mixture is especially suited for well-ground glass stop-cocks upon gas vessels which are to be exhausted and which have therefore to sustain the full pressure of the atmosphere. Such mixtures have been in use for stop-cocks of ordinary burettes in volumetric work during about two years and have given satisfactory results in every way.

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ABSTRACT OF A DESCRIPTION OF A RESPIRATION CALORIMETER FURNISHED BY PROFESSORS ATWATER AND ROSA.[1]

BY C. F. LANGWORTHY.

Received August 6, 1898.

IN 1892 Professors Atwater and Rosa undertook the development of an apparatus for measuring the income and outgo of matter in the animal body. It was proposed, among other things, to study the application of the law of conservation of energy in the animal organism, and plans were made for experiments with man. These required a respiration calorimeter large enough to accomodate a man in comparative comfort for several days at a time and capable of measuring accurately the total income and outgo of matter and energy. The work has been carried out at Wesleyan University, Middletown, Conn., where the facilities of the chemical and physical departments and the mechanical laboratory were made available. The work has been conducted with funds and appliances supplied by the U. S. Department of Agriculture, the Storrs Connecticut Experiment Station, and Wesleyan University.

Considerable time was spent in elaborating the apparatus until it was sufficiently perfected for use in experiments with man. That part which has to do with measuring the income and outgo of matter is similar in principle to the respiration apparatus of

[1] Read at the Sixteenth General Meeting of the American Chemical Society at Washington, D. C., December, 1897.

Pettenkofer and Voit. Many improvements and additions have, however, been made. The appliances for measurement of heat are entirely original. Advantage has been taken of recent progress in electrical science and other branches of physics, and the result is an instrument of remarkable accuracy, notwithstanding its large size.

The portion of the apparatus which has to do especially with respiration experiments has been described in detail in Bulletin No. 44 of the Office of Experiment Stations of the U. S. Department of Agriculture, and the results of four experiments, which include the balance of income and outgo of nitrogen and carbon, are reported in detail. In one of these experiments the subject remained in the respiration chamber for twelve days.

At the meeting of the British Association for the Advancement of Science at Toronto, in 1897, Professor Rosa read a paper describing at some length the special devices used in the measurement of heat and energy produced by the subject in the calorimeter. Brief reference will be made here only to the principal points.

The respiration calorimeter is situated in the basement of the Orange Judd Hall of Natural Science at Wesleyan University.

The respiration chamber is a room or box in which a man may live comfortably during the period of an experiment. The inside dimensions are: Length, 2.15 meters; width, 1.22 meters; height, 1.92 meters. It is provided with conveniences for sitting, sleeping, eating, and working, as well as arrangements for ventilation and for the study of the respiratory products. The chamber consists, in fact, of three concentric boxes, the inner one of metal and the two outer ones of wood. The inner box, of which the inside dimensions have just been given, is double-walled, the inner wall being of sheet copper, the outer of sheet zinc. The two walls are eight cm. apart. This double-walled box is held in shape by a wooden framework between the two metal walls. The inside volume is approximately four and eight-tenths cubic meters.

The limits of this abstract prevent any extended description of the devices used for measuring the incoming and outgoing currents of air or those for measuring the heat produced inside the respiration chamber. A number of improvements suggested

by observation and experiment have been made. For instance, the air as it enters and leaves the chamber is practically freed from moisture by freezing. This greatly facilitates its analysis. The amount of water removed can be accurately determined by weighing.

Since the experiments reported in Bulletin No. 44 were made, meter pumps have been built by the University mechanician, Mr. Blakesley, which render the measurement of the air more simple and accurate. The length of stroke and the volume of air per stroke can be determined, and thus the volume of air drawn through the apparatus may be measured. The pumps are also arranged to deliver an aliquot part of the air for analysis.

In the experiments with man the food, urine, and feces were analyzed by the official methods and the heats of combustion were determined by the bomb calorimeter. No balance of income and outgo of energy was reported in Bulletin No. 44. A considerable number of experiments with man have been made since the publication of that bulletin in which the balance of income and outgo of heat was determined.

The calorimeter is so arranged that the inner and outer metal walls may be kept at the same temperature. When this is done no heat will pass from the inside out or the outside in. The temperature of the inner and outer walls is measured by special devices and the air spaces adjoining the metal walls may be heated or cooled as is shown to be necessary. Since no heat can be lost by passing through the walls of the chamber it only remains to measure the heat generated in it. The means employed are the reverse of those used in heating buildings with hot water. That is, the heat is absorbed by a current of cold water passing through radiators or absorbers. The temperature of the incoming and outgoing currents of water is very carefully determined, and knowing this and the volume of water passing through the absorbers in a given time, the amount of heat produced can be calculated. The current of air necessary for ventilation is kept at the same temperature as it enters and leaves the chamber, hence no heat escapes except by the stream of water and by the latent heat of water vapor passing out with the ventilating current of air.

A number of electrical tests were made of the accuracy of the calorimeter as regards measurement of heat. For this purpose a wire resistance coil was placed inside the chamber. This was connected with wires passing through the wall to the outside and connected with a voltmeter and an ammeter and, in some instances, a Thompson balance. The amount of heat given off inside the apparatus was calculated from the current and was also determined in the water passing through the absorbers. The details of the arrangements and observations are reserved for future publication by the investigator. The results are given in Table I :

TABLE I.

SUMMARY OF ELECTRICAL TEST EXPERIMENTS.

Date.	Duration. Hours and minutes.	Heat as measured.	Capacity correction.	Corrected heat.	Theoretical heat.	Per cent. measured.
	H. M.	Cal.	Cal.	Cal.	Cal.	
March 20, 1897..	13 20	1001.9	—9.0	992.9	989.5	100.3
March 25, 1897..	6 05	528.8	—6.0	522.8	522.1	100.1
March 26, 1897..	7 17	1252.1	—1.2	1250.9	1253.1	99.8
April 30, 1897...	6 00	21.4	0.0	21.4	21.5	99.5
	....	....	....	2788.0	2786.2	100.1

One objection to this use of the electrical method as a test of the accuracy of the apparatus is found in the fact that the conditions were not the same as obtained in an experiment with a man. There was no ventilating current of air through the apparatus, and no water or carbonic acid was given off within it. A number of check experiments were therefore made with ethyl alcohol, and a current of air was passed through the apparatus as in experiments with man. The heat of combustion of the ethyl alcohol was determined by burning it in the bomb calorimeter. These check experiments were made before and after each experiment with a man. In every case the alcohol was burned for a time, generally from three to six hours, before the experiment proper began, the object being to get the temperature of the interior of the apparatus, the moisture content of the air, and the moisture adhering to the inner walls and the heat absorbers as nearly as possible in equilibrium. The attempt was made to have the temperature and moisture content of the air during the last three to six hours of the experiment

the same as in this preliminary period, on the assumption that under these conditions the amounts of moisture in the apparatus would be the same at both times. The quantities of water and carbon dioxide in the air at the beginning and at the end of the experiment were determined in samples of about ten liters drawn out for the purpose.

The apparatus and the conditions of the experiment were such as to permit reasonable uniformity in the flow of the ventilating current of air through the chamber, the rate of combustion of alcohol, the consequent production of carbon dioxide, water vapor, and heat, and the temperature of the interior of the chamber. From 500 to 1,000 cc. of ethyl alcohol was burned in the respiration chamber and the carbon dioxide, water, and heat produced were measured. The results are briefly summarized in Table II.

Considered as results of analyses and of determinations of the heat of combustion of ethyl alcohol, these figures for experiments 1, 2, and 4 would compare with the theoretical figures as shown in Table III.

Note.—Since the above abstract was prepared, a number of additional check experiments with alcohol have been made with the respiration calorimeter, as well as experiments with man, in which the income and outgo of energy was determined, in addition to the balance of income and outgo of carbon and nitrogen. The check experiments and two experiments with man have been reported by Professors Atwater and Rosa in the Tenth Annual Report of the Storrs Connecticut Experiment Station (pages 212–242). The results of the alcohol check experiments are shown in Table IV.

In one experiment with a man the energy of the material actually oxidized in the body was calculated to be 3,864 calories per day. The heat measured by the calorimeter was 3739 calories. In the other experiment with a man the energy of the total material oxidized in the body was 2354 calories per day. The heat measured by the calorimeter was 2329 calories. In other experiments not yet reported the measurements agreed with the theoretical values within one per cent. or less.

The results obtained in the check experiments and in experiments with man are extremely accurate. It would appear that

TABLE II.—SUMMARY OF RESULTS OF ALCOHOL CHECK EXPERIMENTS.

No. of experiment.	Date, 1897.	Duration. Hours and minutes.	Alcohol burned.	Carbon dioxide.		Water.		Heat.	
				Required.	Found.	Required.	Found.	Required.	Found.
		H. M.	Grams.	Grams.	Grams.	Grams.	Grams.	Calories.	Calories.
1	April 27–29	52 30	955.4	1,659.0	1,657.7	1,106.4	1,109.6	5,449.9	5,380.1
2	May 10–11	29 56	798.8	1,387.5	1,385.5	924.8	925.6	4,556.6	4,558.8
3	May 26–27	33 50	505.4	877.6	882.9	585.3	649.7[1]	2,882.9[1]	2,808.5
4	November 2–3	35 9	788.2	1,366.6	1,374.6	912.4	920.9	4,488.1	4,478.8

TABLE III.

DETERMINATIONS OF RESPIRATION CALORIMETER COMPARED WITH THEORETICAL FIGURES FOR CARBON AND HYDROGEN AND HEAT OF COMBUSTION OF ALCOHOL.

	Experiment 1.	Experiment 2.	Experiment 4.	Average.	Theoretical.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Carbon	52.12	52.12	52.54	52.26	52.17
Hydrogen	13.08	13.05	13.16	13.10	13.04
Heat of combustion	98.70	100.00	99.80	99.50	100.00

TABLE IV.—RESULTS OF ALCOHOL CHECK EXPERIMENTS.

Date.	Duration. Hours and minutes.	Alcohol burned.	Carbon dioxide.			Water.			Heat.		
			Theoretical.	Found.		Theoretical.	Found.		Calculated.	Found.	
1898.	H. M.	Grams.	Grams.	Grams.	Per cent.	Grams.	Grams.	Per cent.	Calories.	Calories.	Per cent.
January 6	5 50	112.2	193.7	193.3	99.8	129.8	131.3	101.2	635.6	647.3	101.8
January 24–27	83 44	1607.8	2787.0	2771.0	99.4	1861.3	1884.5	101.2	9153.2	9127.7	99.7
May 9–10	24 00	503.9	867.9	863.7	99.5	586.6	584.8	99.7	2874.3	2862.0	99.6
Total	113 34	2223.9	3848.6	3828.0	99.5	2577.7	2600.6	100.9	12663.1	12637.0	99.8

[1] The excess of water and deficiency of heat are assumed to be due to evaporation of water inside the chamber.

the discrepancies are well within the limits of experimental error. In other words, the respiration calorimeter, although complicated and of such size and construction that a man may remain in it with comfort for a number of days or weeks, will measure carbon dioxide, water, and heat given off in the respiration chamber as accurately as these factors are measured by the usual laboratory methods. The accuracy obtained is much greater than with any similar apparatus with which we are familiar.

Improvements in details are constantly being made. In general, it may be fairly said that the object sought has been accomplished; that is, that the balance of income and outgo of matter and energy of the human subject may be accurately measured during comparatively long periods of time.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

ELECTROLYTIC DETERMINATION OF TIN IN TIN ORES.

BY E. D. CAMPBELL AND E. C. CHAMPION.

Received August 8, 1898.

IN the methods at present in use for the determination of tin in tin ores, the decomposition is effected by fusion with sodium carbonate and sulphur, in order to form sodium sulphostannate, from which the tin is obtained either by precipitation as sulphide with subsequent ignition to the oxide or by electrolytic deposition from the ammonium sulphide or oxalate solution. Some of the objections to the Rose method of precipitation as stannic sulphide and subsequent weighing as stannic oxide are the difficulties of washing the sulphide free from sodium salts, the ignition to stannic oxide without loss of stannic sulphide, and the contamination of stannic oxide with silica.

Electrolytic deposition of tin from the ammonium sulphide solution does not seem to give entirely satisfactory results, for although the tin may be completely precipitated, it is very difficult to obtain complete deposition without at the same time precipitating some sulphur. On the other hand, under proper conditions tin may be very satisfactorily deposited electrolytically from the double oxalate solution; and in the method herewith proposed the principal modification is in the method of convert-

ing the tin from the sulphostannate into the double oxalate. In the method as given by Classen for the conversion of sodium sulphostannate into the double ammonium oxalate, the solution of the sulphostannate is first acidified with sulphuric acid and the tin then oxidized to metastannic acid by means of hydrogen peroxide. The metastannic acid so formed has to be filtered, washed, and dissolved by means of ammonium acid oxalate and oxalic acid, in order to convert it into the double oxalate ready for electrolysis. It was in order to avoid any necessity of precipitating the tin and filtering it out, after it had been once obtained in solution as sodium sulphostannate, that the method given below was perfected. The method in detail, which has given us very satisfactory results on ores tested, is as follows :

Mix one gram of finely ground ore intimately with five to six grams of a fusing mixture made up of equal weights of dry sodium carbonate and sulphur. Place the ore so mixed in a covered porcelain crucible which in turn should be in a larger covered porcelain crucible. This arrangement of double crucibles will prevent oxidation of stannic sulphide during the ignition. Place the crucible upon a triangle and cover with a large Hessian or clay crucible, from which the bottom has been removed, in such a way that the heat from the burner used in the ignition will be kept in, so that the whole of the porcelain crucible will be evenly heated. Raise the temperature of the porcelain crucibles by means of a good burner, such as the Detroit or Fletcher style, to a full red heat, and maintain the temperature for one hour. After allowing it to cool, place the inner crucible in a beaker or casserole and dissolve out the sodium sulphostannate by heating with forty or fifty cc. of water. After complete disintegration of the fused mass, remove the porcelain crucible from the solution and filter out the insoluble oxides and sulphides from the solution, which will contain almost all the tin as sodium sulphostannate. Wash the insoluble residue with hot water. This insoluble residue will usually carry a small amount of tin and must therefore be ignited in the crucible, in which the fusion was performed and after ignition be re-fused as in the first case, with fresh sodium carbonate and sulphur. After fusing the insoluble residue from the first fusion and dissolving out the tin, unite the solutions of sodium sulpho-

stannate. Add to the united solutions of sodium sulphostannate hydrochloric acid, until the solution is slightly acid and the tin has been precipitated as stannic sulphide. Boil down rapidly, until the excess of hydrogen sulphide has been boiled off and the bulk of the solution has been reduced to seventy-five or eighty cc. Add to the hot solution ten cc. of hydrochloric acid (sp. gr. 1.20). Then stir in, a little at a time, sodium peroxide, until the stannic sulphide has been completely oxidized to stannic chloride and the solution has become clear, except for a little sulphur which collects easily on boiling for two or three minutes and can be easily removed by filtering.

The oxidation of stannic sulphide to stannic chloride is very easily effected, requiring usually from two to three grams of sodium peroxide. After oxidizing the stannic sulphide to stannic chloride, boil two or three minutes until the separated sulphur is collected, then filter into a large platinum dish, and wash thoroughly with a little hot water. Add to the solution ammonia until a slight permanent precipitate is obtained, then fifty cc. of a ten per cent. solution of acid ammonium oxalate. This will give a clear solution from which the tin is easily deposited.

Electrolyze over night with a current N. $D._{100} = 0.10$ ampere with an electromotive force of four volts. This current can be obtained from two storage cells using suitable resistance. In the morning the tin will be found to be completely precipitated as a pure white, firmly adherent metal upon the platinum dish. When eight volts E. M. F. were used the deposit was found to be more strongly crystalline and less firmly adherent than when lower voltage was employed. When the tin is completely deposited, disconnect and wash the tin first with water, then with alcohol. Drain off the latter as completely as possible and dry between 80° and 90° C. If the deposited tin is found to have small crystals of ammonium oxalate adhering to it, they may be easily removed by washing with a little warm water before the final washing with alcohol. After weighing the platinum dish containing the precipitated tin, the latter is dissolved off by heating with a little hydrochloric acid and the weight of the platinum dish obtained after washing and drying as before.

In electrolytic determination of metal where they are deposited in platinum dishes, the results will be found to be much more satisfactory, if duplicate determinations are made in platinum dishes of practically the same size, and the dishes are washed, dried, cooled, and weighed under the same conditions, each dish serving as a counterpoise for the other. By using dishes in this way, variations of weight due to atmospheric changes may be reduced to a minimum and the results made more accurate than when a dish is weighed alone.

ANN ARBOR, MICH., June 21, 1898.

[CONTRIBUTIONS FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

ON THE INFLUENCE OF SILICON UPON THE HEAT OF SOLUTION OF COKE CAST IRONS.

BY E. D. CAMPBELL AND WM. E. HARTMAN.

Received August 8, 1898.

THE principal object of the following research was to determine if any thermochemical evidence could be obtained indicating a change in the condition in which silicon exists in cast iron, this change being due to differences of the temperature at which the iron is made. It is well known that when the temperature in a blast-furnace passes a certain point, namely, that at which No. 1 foundry iron is made, the color of the cast iron produced changes somewhat as the temperature of the furnace rises. This change continues until it reaches the temperature at which silvery or glazed iron is made, when there is a very abrupt change in the appearance and properties of the iron. It was thought that the appearance peculiar to silvery iron might be due to a change of form in which the silicon exists, and that this change might be indicated thermochemically.

The cast irons used in this work, with the exception of the two ferrosilicons, were all made in the same blast-furnace from approximately the same stock. They were selected from among a large number of samples with a view to obtaining a regularly increasing per cent. of silicon as the temperature at which the iron was produced increased, this temperature being judged by the grade of the iron.

The chemical analyses upon these irons included the deter-

minations of graphitic carbon, manganese, phosphorus, silicon, and total iron. In addition, after the samples had been dissolved in the calorimeter, the amounts of iron and phosphorus in the insoluble residue were determined. From these two latter results the amount of iron oxidized to ferrous chloride and of phosphorus oxidized to phosphoric acid could be found. All the manganese passes into solution as manganous chloride.

In the calorimetric determinations, a one-gram sample was used in all cases. The solvent was a solution of ammonium copper chloride made up in the molecular ratio,

$$(NH_4Cl)_2CuCl_2 : 50H_2O,$$

but with the addition of 0.84 per cent. of free hydrochloric acid. It was found that when a sample of pure carbide of iron, of the empirical formula CFe_3,[1] was treated with strictly neutral ammonium copper chloride solution, there was apparently no action at all, the carbide remaining unaltered. The addition of only 0.09 per cent. free hydrochloric acid induced marked action, while with 0.84 per cent. of free acid solution of one gram was complete in two minutes. Pure water acidified with 0.84 per cent. of free acid was without appreciable action upon the pure carbide of iron. Owing to the greatly increased chemical activity of a slightly acid solution, compared with that of a strictly neutral one, it was thought best to use the former, as there seemed to be no danger of direct reaction between the hydrochloric acid and the metal under treatment.

The rise of temperature of the solution in the calorimeter was determined by means of a Beckmann thermometer, graduated in hundredths of a degree, the graduations being large enough so that with the aid of a reading glass, readings could be made in thousandths of a degree, with an error not exceeding two thousandths. The rise of temperature in the calorimeter varied for the different samples between 2.780° and 3.715°.

Owing to the varying lengths of time required for solution of the different samples, corrections were made in all cases for the loss by radiation. In each calorimetric determination readings were made at the end of each minute until a fall in the thermometer indicated complete solution; and corrections were

[1] "A Pure Carbide of Iron"—*Am. Chem. J.*, **18**, 836.

made for loss according to the difference in temperature at the time of each reading. The rate of loss by radiation for varying temperatures was determined for differences of 1°, 2°, and 3° between the initial and final temperatures; and it was found that for twenty-five minutes, the rate of loss by radiation for any given difference, was constant. For a difference of 3° between the initial and final temperatures the rate of loss was 0.015° per minute. The correction that had to be applied because of this loss varied between 9.6 and 20.1 calories with the exception of one case in which the solution required twenty-two minutes, necessitating a correction of ninety-eight calories. It was also found that a second correction had to be made owing to the slow oxidation of the cuprous to cupric chloride by the air dissolved in the solution. This oxidation takes place most rapidly during the first ten minutes, after which the rate falls off as the amount of dissolved air present, diminishes. The correction due to this oxidation amounts to six-tenths of a calorie per minute for the first ten minutes, which amount falls to 0.36 calorie during the succeeding five minutes, and to 0.24 calorie at the end of fifteen minutes from the start. This correction was determined by dissolving 1.132 grams of pure copper, the chemical equivalent of one gram of pure iron, and noting the slow, continuous rise of temperature after the copper was completely in solution as cuprous chloride.

In the reduction of the results to absolute calories, since we had not access to apparatus for determining accurately the specific heat of a solution, resort was made to an indirect method for the determination of the water equivalent of our solvent. The following data were used: specific heat of glass, 0.177; specific heat of mercury, 0.033: specific heat of iron, 0.111; calories evolved by one gram of iron when dissolved in ammonium copper chloride, 719.3. This last figure was obtained from the heats of formation of ferrous, cupric, and cuprous chlorides as given in Thomsen's "Thermochemische Untersuchungen," 3, 506.

$$Fe + 2CuCl_2 = FeCl_2 + 2CuCl,$$
$$Fe + (2 \times 62710) = 99950 + (2 \times 32875),$$
$$\text{or } 40280 \div 56 = 719.3 \text{ calories.}$$

Figuring from these data, by dissolving one gram of pure iron and dividing 719.3 by the rise of temperature, correcting for loss by radiation and for gain by oxidation of cuprous chloride, the water equivalent of the solution used and containing vessel, thermometer, and stirrer could be calculated. By subtracting the water equivalent of these latter, the specific heat of the solvent was found. This gave 0.8226 as the specific heat of the solution used.

Since the cast irons, with the exception of the ferrosilicons which were nearly free from manganese, contained from 0.46 to 1.05 per cent. of manganese, a correction had to be made for the heat evolved in its solution. From the equation:[1]

$$Mn + 2CuCl_2 = MnCl_2 + 2CuCl,$$
$$Mn + (2 \times 62710) = 128000 + (2 \times 32875),$$
$$\text{or } 68330 \div 55 = 1242.3 \text{ calories for one gram.}$$

This would require a correction of 1.24 calories for each 0.001 gram of manganese.

The corrections necessitated by the presence of manganese varied between 6.3 and 15.6 calories. A similar correction was introduced on account of the presence of phosphorus. The total phosphorus in the cast irons varied between 1.120 and 1.424 per cent.; but the amount oxidized was from 0.325 to 0.656 per cent. So correction was made only for the phosphorus oxidized to phosphoric acid.

$$P_2 + 10CuCl_2 + 5H_2O + Aq. = P_2O_5Aq. + 10CuCl + 10HCl,^2$$
$$P_2 + (10 \times 62710) + (5 \times 68360) =$$
$$405500 + (10 \times 32875) + (10 \times 39315).$$

or $158500 \div 62 = 2556.5$ calories for one gram.

This would require a correction of 2.56 calories for 0.001 gram phosphorus, or from 9.5 to 18.8 calories for the various samples dissolved.

In determining the amount of heat evolved by the oxidation of the silicon present, the heat of solution of one gram of the sample was found, correction being made for the loss by radiation and gain by oxidation of cuprous chloride. The number of calories per gram of iron dissolved was calculated by dividing

[1] Thomsen's Thermochemische Untersuchungen, **3**, 506.

[2] *Ibid*, **3**, 506; **2**, 398; **2**, 409; **3**, 506; **2**, 399.

this first figure by the per cent. of iron actually obtained in solution. From the figure thus derived was subtracted the amount of heat due to the manganese and the phosphorus oxidized with one gram of iron, in addition to 719.3 calories, the heat evolved by solution of one gram of pure iron. The remainder thus obtained was assumed to be the heat evolved by the oxidation of the silicon accompanying one gram of iron dissolved. From the heat due to the oxidation of the silicon accompanying one gram of iron, the number of calories for one gram of silicon was then calculated.

The calorimetric results obtained from the cast irons examined, are best shown in the subjoined table:

Grade of iron.	Per cent. of silicon.	Calories for one gram of sample.	Time in minutes required for solution.	Calories for one gram of iron dissolved.	Calories from oxidation of the silicon with one gram of iron.	Calories from oxidation of one gram of silicon.
Ferrosilicon	13.63		No action.			
Ferrosilicon	11.79	982.3	22	1163.9	444.6	3183
Silver-gray cast iron	6.16	820.4	7	968.9	215.2	2959
Silver-gray cast iron	4.69	765.6	6	900.4	150.2	2760
No. 2 soft cast iron	4.15	769.6	3	880.5	137.9	2904
No. 1 soft cast iron	3.55	765.9	4	873.1	133.6	3303
No. 1 foundry cast iron	3.13	732.4	3	835.0	91.3	2561
No. 2 foundry cast iron	2.56	720.6	5	817.9	79.5	2731
No. 3 foundry cast iron	2.05	710.9	3	797.0	59.7	2598
Gray forge cast iron	1.40	690.5	5	781.1	42.4	2677
Mottled cast iron	0.89	672.7	11	741.3	—2.9	—298
Mottled cast iron	1.33	700.8	3	868.4	28.9	1989
Mottled cast iron	2.35	730.9	3	812.1	64.8	2822

A study of the above table seems to indicate the following facts:

First: When either from a sufficiently high temperature of the blast-furnace at the time the iron is made or from the presence of a moderate amount of silicon, probably about one and four-tenths per cent., the carbon is nearly all in the graphitic or graphitic temper form; then the heat evolved by the oxidation of the silicon is proportional to the amount of silicon present.

Second: When from a low temperature in the furnace accom-

panied by low silicon the carbon is largely in the combined form; then the heat rendered sensible is very much diminished owing to the large amount of heat necessary to decompose the compounds of iron and carbon, or possibly compounds of iron, silicon, and carbon, or of carbon and silicon.

Third: Since from the equation:

$$Si + 4CuCl_2 + 2H_2O = SiO_2Aq + 4CuCl + 4HCl,$$

$$Si + (4 \times 62710) + (2 \times 68360) =$$

$$207400^1 + (4 \times 32875) + (4 \times 39315),$$

$$\text{or } 108600 \div 28.4 = 3824,$$

we see that the oxidation of one gram of silicon alone evolves 3824 calories, and the results obtained by dissolving cast irons give a maximum of 3303 calories, it is evident that the compound of silicon with iron must have a very considerable heat of formation. This would indicate as a minimum for the equation:

$$Si + Fe_n = SiFe_n + 14900 \text{ calories.}$$

If the mean of all the determinations, excluding the results on the two mottled irons containing high carbon, is taken, then the heat of formation would be increased to 27,700 calories.

Fourth: When the per cent. of silicon is sufficient or nearly sufficient to correspond with the empirical formula $SiFe_2$, the compound is insoluble in ammonium copper chloride. This is shown in the case of the higher silicon ferrosilicon.

These results are not in complete agreement with those obtained by F. Osmond,[2] but the differences may be ascribed either to the fact that he used samples of iron very low in all elements other than silicon, or to the fact that he used strictly neutral ammonium copper chloride instead of a slightly acid solution, which we have shown is much more active than the former.

[1] *Compt. rend.*, 113, 475—"Recherches calorimetriques sur l'etat du silicium et de l'aluminium dans les fers fondus," par F. Osmond.

[2] *Compt. rend.*, 113, 474.

ON THE OCCURRENCE OF HYDROGEN SULPHIDE IN THE NATURAL GAS OF POINT ABINO, CANADA; AND ON A METHOD FOR THE DETERMINATION OF SULPHUR IN GAS MIXTURES.[1]

By Francis C. Phillips.

Received July 19, 1898.

ON the northern shore of Lake Erie, ten miles west from Buffalo, a narrow promontory extends for a distance of about two miles out into the lake. This promontory, known as Point Abino, forms the southern extremity of an important region of natural gas production from which a large part of the gas used in Buffalo at the present time is derived.

In 1892 a well was drilled by the Provincial Natural Gas Company near the extremity of Point Abino, to a depth of 600 feet. Gas was found in this boring at 550 feet below the surface, and again fifty feet deeper, or at the base of the Niagara limestone. The well has maintained its productiveness with little loss of pressure since the date of its drilling.

As regards chemical composition, the gas derived from this limestone at Point Abino differs in a remarkable manner from that which is usually found in the Devonian rocks of western Pennsylvania in the fact that it contains hydrogen sulphide, easily recognizable by its strong odor, by its action upon polished surfaces of silver and copper, and by the presence of sulphur dioxide among the products of its combustion. Two other wells on Point Abino yield gas of similar character (known locally as "sulphur gas") from the same geological formation.

It is common in drilling wells into the Niagara limestone in this region to find natural gas impregnated with hydrogen sulphide, sometimes occurring in small quantities, apparently stored in cavities from which it soon escapes and is exhausted; in other cases the sulphur gas, when once it is tapped, may continue to flow for an indefinite period.

In cutting a sewer tunnel through the limestone, fifty to sixty feet under the city of Niagara Falls, and extending about one mile from Twenty-third street to the river, hydrogen sulphide

[1] Read at the Washington meeting of the American Chemical Society, December, 1897.

was frequently encountered, and was the cause of much inconvenience to the workmen, requiring the construction of ventilating shafts for its removal. The occurrence of this gas was always accompanied by a strong flow of dark-colored water.

Mr. W. A. Brackenridge, resident engineer for the Cataract Construction Company, informs me that hydrogen sulphide was found at a depth of about sixty feet in excavating for the wheel pit and tunnel shaft of this company at Niagara Falls. Patches of gypsum were often found about ten feet above the gas-bearing stratum. If this gas is allowed to come in contact with the polished metal surfaces about the power house they are rapidly blackened. Natural gas of the same character has been found near Fort Erie, at several places between Buffalo and Point Abino, and also at Port Colborne on Lake Erie, twenty miles west from Buffalo. Water well drillers state that they often strike sulphur gas at Chippewa, south of Niagara Falls. Southeast from Buffalo, from four to six miles, hydrogen sulphide occurs in the Niagara limestone of the West Seneca field, and at Alden, eighteen miles east from Buffalo. The sulphur gas is found in wells distributed over a territory extending irregularly for about forty miles east and west, and about twenty miles north and south.

Natural gas occurs in the region at three other horizons below the Niagara limestone; namely the Clinton limestone, the Medina sandstone, and the Trenton limestone, which latter rock was reached at a depth of 2940 feet in a well drilled six miles north of Point Abino. The Niagara limestone seems, however, to be the only one of these formations which yields gas containing hydrogen sulphide.

On September 2, 1896, I visited the well at Point Abino, and by the courtesy of Mr. E. Coste, engineer for the Provincial Natural Gas Company, was enabled to conduct some tests of the gas upon the spot and to collect samples for analysis. Of these tests made at the well and the results obtained, the following is a brief summary:

On leading the gas through an alkaline lead acetate solution, a heavy black precipitate was at once produced.

An ammoniacal cadmium chloride solution yielded a bright

yellow precipitate. The odor of hydrogen sulphide was very strong.

It seemed to be of interest to ascertain whether organic sulphur compounds were present among the hydrocarbons of this gas. Accordingly, a stream of the gas was caused to bubble through an alkaline lead acetate solution, in order to absorb hydrogen sulphide, and then through an alcoholic solution of mercuric chloride. The experiment was continued for six hours at the well. Methyl, as well as ethyl sulphide would have caused a precipitation in the mercuric chloride solution, if present even in very small quantity. The solution was found to remain clear. The absorbent solutions were returned to the laboratory to be further tested. The alkaline lead acetate solution was warmed upon a water-bath while a current of nitrogen was passed through the flask and into an alcoholic solution of mercuric chloride. In this latter solution no precipitate appeared, nor was any odor attributable to a sulphur ether observed. These tests seemed necessary, as a volatile sulphur ether might have condensed unchanged in the lead acetate solution during the passage of the gas in the trials which were made at the well. The nitrogen stream was used in order to evaporate any traces of such condensed sulphur compound, should there be any such, and carry its vapor over into the reagent solution.

In order to test for methyl mercaptan advantage was taken of the fact that its vapor is readily absorbed by an alkaline lead acetate solution and is again evolved when the liquid is acidulated and warmed. If the escaping vapors are led (by a nitrogen stream) into a solution of palladium chloride a cinnamon-colored precipitate is produced. This test was performed but the results were negative. The odor of mercaptans was not noticeable. It is of course possible that experiments with still larger volumes of gas might have disclosed the presence of traces of such organic sulphur compounds.

The vapors of methyl and ethyl sulphide, even if present in a gas in quantity insufficient to produce a precipitate in mercuric chloride solution, are absorbed by the solution, and impart to it their characteristic odor, so that this reagent may in such manner serve for the detection of very slight traces not otherwise recognizable.

In order to test for the presence of carbon monoxide the gas, as it flowed from the well, was passed (1) through lead acetate solution containing a large excess of sodium hydroxide to remove carbon dioxide and hydrogen sulphide, (2) through lime-water, in order to maintain control of the efficiency of the first solution, (3) through palladium chloride solution, and (4) through lime-water. When present in a gas mixture, even in traces, carbon monoxide is easily recognized by this method, the second lime-water becoming milky as a result of the oxidation of the carbon monoxide by the palladium chloride. The palladium chloride is simultaneously reduced, yielding a black precipitate of finely divided metal.[1]

In testing for free hydrogen the method I have described in the *American Chemical Journal*, **16**, 259, was used. The gas freed from hydrogen sulphide and dried by phosphoric anhydride, was passed through a tube containing dry palladium chloride and then into silver nitrate solution. Dry palladium chloride is quickly reduced in the cold by free hydrogen, with formation of hydrogen chloride, which then produces its characteristic effect upon the silver nitrate solution.

The results of these tests, conducted at the well during about six hours, were negative, and the conclusion seems justified that carbon monoxide and free hydrogen do not occur in the Point Abino natural gas in recognizable quantity.

Tests for ethylene were made in small portions of the gas brought back to the laboratory for the purpose, but with negative results. Determinations of hydrogen sulphide were made by agitating a measured volume of the gas with an alkaline solution of lead acetate, in a bottle fitted with a rubber cork, traversed by inlet and outlet tubes having stop-cocks, and by a burette for the introduction of the reagent solution. This part of the work was carried out at the well, due account being taken of the temperature and barometric pressure. The bottle used was of 1890 cc. capacity. The precipitated lead sulphide was returned to the laboratory, its sulphur oxidized to sulphuric acid, and from the weight of barium sulphate obtained the proportion of hydrogen sulphide in the original gas was calculated.

[1] For details of this method as applied to natural gas see *American Chemical Journal*, 16, 275.

The results of four determinations made in this manner were 0.76, 0.73, 0.75, and 0.72 per cent.

Nitrogen was determined by combustion of a measured volume of the gas (about 150 cc.) over copper oxide, and measurement of the residual gas over mercury. This residue may include other inert gases besides nitrogen, but these have been classed together in the present analysis. The method used for collection of this inert residue is one requiring a somewhat complicated form of apparatus. Its details will be described in a later paper.

Carbon and hydrogen were determined gravimetrically, by weighing the carbon dioxide and water produced when a measured volume of the gas was burned over copper oxide. For this purpose glass cylinders holding from 350 to 400 cc. were filled with the gas at the well.

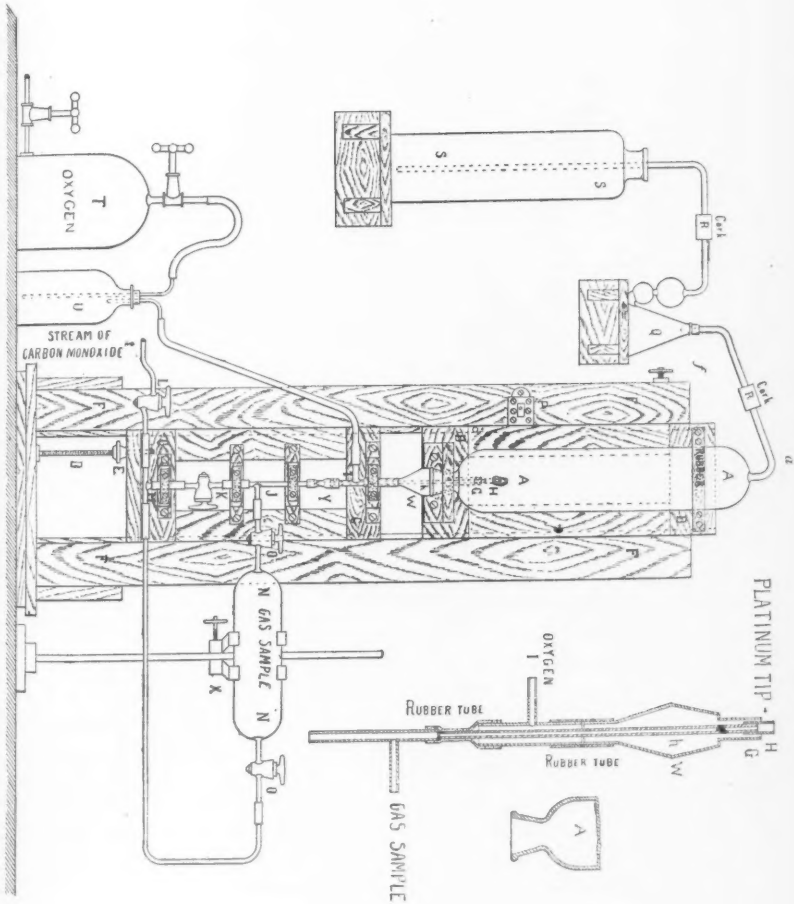
Results of analysis of natural gas from the Point Abino well.

	Per cent.
Hydrogen sulphide	0.74
Nitrogen	2.69
Carbon dioxide	trace
Carbon monoxide	0
Hydrogen	0
Ethylene	0
Hydrocarbons of the paraffin series	96.57
	100.00

The percentage composition of these paraffins by weight was:

	Per cent.
Hydrogen	24.10
Carbon	75.90
	100.00

With a view to greater certainty in the determination of hydrogen sulphide it seemed desirable to employ a method by which the gas could be burnt, and the sulphur collected as barium sulphate. Accordingly, a process was devised for the combustion of a measured volume of the gas in an oxygen atmosphere, absorption of the sulphuric or sulphurous acid produced, and weighing of the sulphur as barium sulphate. Such a method is not new in principle, having been proposed by various authors for the determination of sulphur in gases. As adopted for use in the present instance the method may be described as follows:


OXYGEN
T
STREAM OF CARBON MONOXIDE
S
Cork
R
RUBBER
A
GAS SAMPLE
N
X
O
OXYGEN
RUBBER TUBE
RUBBER TUBE
PLATINUM TIP
H
G
GAS SAMPLE

The gas sample is contained in the vessel *N* (which may be replaced by a larger vessel if necessary). It is burnt from a narrow glass tube *h* surmounted by a roll of thin platinum foil *H*, in a light blown glass cylinder *A*, which is about forty cm. long and about ten cm. wide. The cylinder is closed below by a ground stopper *W*. This stopper is hollow and carries the narrow tube of about one and one-half mm. bore supplying the gas to be burnt. The narrow tube passes up through one of larger diameter which receives oxygen by way of the side tube *I* from a holder *T* and delivers it just below the flame of burning gas. As is shown in the sketch of the stopper *W* and its connections, the burner tubes are arranged concentrically, the oxygen issuing from the wide tube *G* and encircling the flame of the gas burning at the tip *H*. The rate of flow of the oxygen is approximately indicated by the rapidity of its bubbling through water in the bottle *U*. It seemed desirable to effect the expulsion of the gas from the sample vessel into the cylinder where it is to be burnt without the use of water, which by reason of its solvent power might absorb and partially remove those constituents of the gas which are to be determined. Mercury is out of the question. A gas appeared preferable and carbon monoxide was employed for the purpose. The carbon monoxide is contained in a gasholder and enters by the tube *L*, passing upward by *K* and *h* to the platinum tip *H*, where it is ignited. The combustion cylinder, which is mounted on the movable frame *BB*, is then lowered over the ignited carbon monoxide jet and clamped in position by the screw *f*. The outlet tube *a* is connected with the flask *Q* containing a solution of sodium carbonate to which some bromine has been added. The lower sliding frame *CC* can be raised or lowered by the nut *E* moving upon the fixed screw *D*. The carbon monoxide jet being ignited and the oxygen supply by way of *I* being adjusted so as to insure a steady flame, the stop-cocks *OO* are opened and then *K* is closed. The carbon monoxide then goes by way of the gas sample vessel to the jet, driving out the contained gas and carrying it into the combustion cylinder, where it is burnt. Many liters of gas may be burnt in this manner without danger of the flame becoming extinguished. The sodium hypobromite solution into which the products of the combustion have passed contains the sulphur

as sodium sulphate, and, after acidulation and evaporation, may be used for the determination of sulphur as barium sulphate. After the combustion is finished the apparatus is tilted down, the cylinder is rinsed, and the rinsings added to the contents of the flask *Q*. The large bottle *S* containing a few drops of bromine water, which is renewed from time to time during the process, is used to insure complete absorption of products of combustion of the sulphur. The connections *RR* consist of corks soaked in melted paraffin or spermaceti, rubber being objectionable on account of the sulphur which it contains.

The combustion of natural gas, or other gas rich in hydrogen, leads necessarily to the production of much water. This water is partly condensed at first, but as the temperature of the cylinder rises and evaporation is accelerated, the water vapor increases, and impairs the stability of the flame, which may flicker and become extinguished, even when the oxygen supply is apparently sufficient. The carbon monoxide, by diluting the products of combustion, tends to prevent condensation of steam and renders the flame more steady and more easily controlled. If very large volumes of gas are to be burned carbon monoxide cannot be used as it renders the process too slow, and in such case measurement of the gas must be effected by meter. No carbon monoxide is then required. Natural gas may be burned in this apparatus at the rate of a liter in twelve minutes.

Experiments have shown that the position of the gas sample vessel, whether vertically or horizontally placed, makes little difference, as the carbon monoxide rapidly mixes with the gas in the sample vessel and the two emerge together at the burner.

There appeared to be some danger that carbon monoxide made from oxalic acid by heating with sulphuric acid might contain volatile sulphur compounds. Carbon monoxide, prepared from chemically pure sulphuric acid and recrystallized oxalic acid, was found after passage through sodium hydroxide solution, to yield no sulphuric acid when ten liters were burned in the apparatus described.

Nitrous oxide may be substituted for oxygen in the process, and being readily obtainable in liquefied form, proves more convenient. During combustion in nitrous oxide higher oxides of nitrogen are formed in quantity sufficient to give a bright orange

color to the gaseous contents of the combustion cylinder. The conditions are then very favorable to the complete oxidation of gaseous sulphur compounds.

The Point Abino gas well was visited again on September 3, 1897, when the tests made a year ago were repeated, and other samples taken. Determinations of sulphur were made by the method of combustion above described. Determinations of hydrogen sulphide were also made by treatment of a known volume of gas at the well with alkaline lead acetate solution. The precipitated lead sulphide having been returned to the laboratory, its sulphur was converted by oxidation by means of potassium chlorate and hydrochloric acid into sulphuric acid, and precipitated and weighed as barium sulphate.

	By combustion in oxygen and weighing as barium sulphate.	By precipitation as lead sulphide and conversion into barium sulphate.
	Percentage by volume.	Percentage by volume.
Hydrogen sulphide.....	0.80	0.77
	0.83	0.86
	0.82	0.80
	0.82	
	0.83	

The only important difference as regards composition between the natural gas from the Niagara limestone and that from the Devonian measures of western Pennsylvania consists, apparently, in the hydrogen sulphide which the former gas contains. If the sulphur compound be removed the residual gas is hardly distinguishable in composition from the natural gas of other regions. There appears to be reason for regarding the sulphur gas of Point Abino as natural gas which has received an addition of hydrogen sulphide derived from some local source. The same process which has produced natural gas in other regions has probably yielded this gas but the hydrogen sulphide which it contains may be derived from a different source, and may have been of more recent origin.

The occurrence of hydrogen sulphide in the Niagara limestone is no doubt connected with that of gypsum, which abounds so largely throughout the region. Gypsum has been quarried near Buffalo and is often found scattered through the limestone

in cavities. In artesian borings many alternations of limestone and gypsum are often encountered. Considerable masses of this mineral are found near Sherkston, north of Point Abino, and near Niagara Falls it occurs abundantly in the limestone.

If a genetic relationship exists, as is suggested by their association, it is difficult to determine whether the hydrogen sulphide, by oxidation in presence of limestone, has produced gypsum, or whether the gypsum has by decomposition yielded hydrogen sulphide. If hydrogen sulphide has undergone oxidation there seems to be reason to suppose that the process must have occasionally remained incomplete when occurring at great depths, and have resulted in the setting free of sulphur. Sulphur does not appear to occur native in the region. If the hydrogen sulphide has penetrated from greater depths to undergo oxidation in the higher strata it should be found more abundantly in the lower gas-bearing rocks, instead of being confined to the uppermost of these, the Niagara limestone.

On the other hand, the production of hydrogen sulphide from gypsum would seem to require an exposure to high temperature in presence of hydrocarbons—conditions which cannot have occurred. No one of the constituents of natural gas could, at temperatures existing in the stratified rocks of the region, have produced hydrogen sulphide by its action upon gypsum.

The Point Abino well produces, according to Mr. E. Coste, engineer for the Provincial Natural Gas Company, 1,000,000 cubic feet per day, and of this amount 7,000 cubic feet are hydrogen sulphide, corresponding to 600 pounds of sulphur, or 115 tons in one year. It is true that the well is not being drawn upon constantly up to its full capacity, but as it represents only one among the many outlets from which the sulphur gas escapes, it is evident that a very large quantity of sulphur, either in form of hydrogen sulphide, or burnt in furnaces to sulphur dioxide, is making its way annually into the atmosphere in the region of Buffalo and Niagara Falls.

LABORATORY OF THE
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CERTAIN ALKALOIDAL PERIODIDES, AND THE VOLUMETRIC ESTIMATION OF ALKALOIDS AS HIGHER PERIODIDES.[1]

By A. B. Prescott and H. M. Gordin.[2]

THE PERIODIDES IN RESPECT TO COMPLETENESS OF PRECIPITATION.

IN aqueous solutions of salts of the alkaloids, one of the most delicate of qualitative reagents is iodopotassium iodide. Wormley gives the limit of this precipitation, for the chief medicinal alkaloids, as from $\frac{1}{50000}$ to $\frac{1}{100000}$ of a grain of the alkaloid in one grain of water; that is, from 0.0000013 to 0.0000007 gram in one cc. of water.[3] The precipitate is not appreciably soluble in excess of the reagent, an advantage over several other qualitative precipitations of alkaloids in general. In some cases the precipitate is appreciably soluble in excess of the alkaloidal salt, and this condition is one most easy to avoid. The potassium iodide solution of iodine was recommended as a reagent for alkaloids by Bouchardat, a medical writer in Paris, in 1839.[4]

As a volumetric solution, the decinormal solution of iodine with potassium iodide was first proposed by Wagner, in 1861,[5] and the decinormal strength is generally the most suitable for volumetric use.

HISTORICAL AS TO THE FORMATION OF PERHALIDES IN GENERAL.

The formation of the alkaloidal periodides was first made a subject of systematic observation by Jörgensen, at Copenhagen,

[1] The portion of this article which concerns atropine was given in substance in this Journal, **20**, 329, under the title "Atropine Periodides and Iodomercurates," by H. M. Gordin and A. B. Prescott (reprints). Also that concerning morphine and opium, except the "Results of Opium Assay," appeared in Kremers' *Pharmaceutical Archives*, June, 1898, **1**, 121, under the title "A Volumetric Assay of Opium," by H. M. Gordin and A. B. Prescott (reprints).

[2] In the work of Research Committee D, Section 2, Committee on Revision of the Pharmacopeia of the United States.

[3] Microchemistry of Poisons, 1885, Tabular View.

[4] Bouchardat, 1839: *Compt. rend.*, **9**, 475; *L'Institut*, **7**, 358. This precipitation, however, was proposed as an antidote for strychnine, in cases of poisoning of dogs. Further, see Donné: *Ann. chim. phys.* (2), **38**, 82.

[5] R. Wagner: Dingler's *poly. J.*, **161**, 40; *Ztschr. anal. Chem.*, **1**, 102.

in 1869,[1] and the masterly researches of this Danish chemist, extending over nine years, afford a model of logical inquiry into chemical structure. A still wider study of all periodides and some other perhalides of organic bases was commenced in 1887 by Prof. Geuther[2] of Jena, but was cut short by his death in 1889. Among various periodides reported of later years have been picoline periodides by Wm. Ramsay in 1878;[3] cesium and rubidium periodides by Wells, and others, in 1893;[4] iodonium periodides by Victor Meyer in 1894;[5] sulphon periodides by Kastle in 1894;[6] periodides of diazo bodies by Hantsch in 1895;[7] halogen addition-products of the anilides by Wheeler and others in 1896-97;[8] perhalides of aliphatic amines by Norris in 1898;[9] mixed perhalides of alkyl anilines by Samtleben in 1898.[10]

In this laboratory since 1895 the perhalides and various double halides of pyridine have been obtained,[11] also the perhalides of caffeine,[12] and work on picoline perhalides is in hand. In the course of work upon an entirely different inquiry, a new order of perhalides has just been obtained, a periodide of bromtriphenylmethane.[13]

It is of interest to inquire what classes of compounds are liable to the formation of perhalides, and this inquiry has a special interest when it is proposed to estimate a single class of compounds, in vegetable drugs or their extracts, by formation of periodide. In general terms the reply is easily given, that

[1] Jörgensen, 1869-1878: *J. prakt. Chem.* (2), **2**, 347, 433; **3**, 145, 328; **14**, 213, 356; **15**, 65, 418; **16**, 352; *Ber. d. chem. Ges.*, **2**, 460.

[2] A. Geuther: *Ann. Chem. Pharm.* (Liebig), **240**, 66-91, with lists of the organic periodides previously obtained.

[3] *Phil. Mag.* (5), **2**, 269; **4**, 241; **6**, 19.

[4] *Am. J. Sci.* (3), **44**, 42; **43**, 17.

[5] *Ber. d. chem. Ges.*, **27**, 1594.

[6] *Am. Chem. J.*, **16**, 116.

[7] *Ber. d. chem. Ges.*, **28**, 2754.

[8] *Am. Chem. J.*, **18**, 85; **19**, 672.

[9] *Am. Chem. J.*, **20**, 51.

[10] A. Samtleben: *Ber. d. chem. Ges.*, **31**, 1141.

[11] Prescott, the Periodides: This Journal, **17**, 775; *Pharm. Rundschau*, **13**, 233. Prescott and Trowbridge, Periodides of Pyridine: This Journal, **17**, 859. Flinterman and Prescott, Dipyridine Methylene Dibromide. *Ibid*, **18**, 28. Prescott, Pyridine Alkyl Iodides: *Ibid*, **18**, 91. Trowbridge, Periodides of Pyridine: *Ibid*, **19**, 322. Trowbridge and Diehl, Halides and Perhalides of Pyridine: *Ibid*, **19**, 558.

[12] Gomberg, Perhalides of Caffeine: This Journal, **18**, 347-378.

[13] See paper by Gomberg read at Boston meeting of the American Chemical Society, August, 1898, and to be published in a subsequent number of this Journal.

periodides are limited to the organic basis, that is the more or less basal compounds of the nitrogen family of elements, and the inorganic alkalies. It is remarkable that the iodonium compounds yield periodides, which is quite in accord with the claim of Victor Meyer that in these bodies iodine itself strangely serves (with the benzene ring) as a base-forming element like a member of the nitrogen family. This view is supported further by Gomberg's production at this time of a periodide of a triphenylmethane derivative, as cited just above.

At present it seems highly improbable that any plant constituent other than the alkaloids, in the larger sense of organic bases, are of the sort of bodies which can form periodides in precipitation. Moreover, Wagner's reagent is used in a qualitative way along with plant analysis to an extent likely to call attention to any interference with its use for alkaloids. From the work of Wheeler it is evident that periodides may be formed by acid amides, but probably not by precipitation in dilute solutions. The formation of iodonium periodides, and a sulphone periodide, indicate that the limits of formation of perhalides cannot yet be declared, and it will be well for analysts to be watchful of new developments.

HISTORICAL AS TO ANALYTICAL USE OF PERIODIDES.

The volumetric use of a potassium iodide aqueous solution of iodine dates from Wagner in 1861,[1] and the solution in decinormal strength of iodine is named Wagner's reagent.

This iodine solution was tried briefly by Schweissinger in 1885,[2] and at length by Kippenberger in 1895,[3] but both seem

[1] R. Wagner, 1861: Ding. *poly. J.*, **161**, 40; *Ztschr. anal. Chem.*, **1**, 102. Wagner wisely avoided washing the precipitate, but he failed to add the solution of alkaloid to that of iodine: "Man versetzt die Losung der Basen, deren Menge man bestimmen will, mit überschüssiger Iod lösung, filtrirt und bestimmt in einem gemessenen Theil des Filtrats mit unterschwefligsaurem Natron das überschüssige Iod." As periodides had not then been prepared and analyzed, the iodine factors of Wagner were empirical, and, as the higher periodides are not invariably the sole products when iodine solution *is added to* the alkaloid solution, the factors adopted proved unsatisfactory. It is noteworthy that "Mayer's reagent" was so nearly contemporaneous with Wagner's, in publication. The potassium mercuric iodide method of volumetric estimation dates from 1862: *Proc. Am. Pharm. Assoc.*, 230; *Am. J. Pharm.*, **35**, 20; *Chem. News*, **7**, 159; **8**, 177, 189. Of special American interest is Dr. F. Hoffmann's biography of Ferdinand F. Mayer as a New York chemist (*Pharm. Rundschau*, 1894, **12**, 125), and of more general interest, Prof. Schaer's history of Mayer's alkaloid reagent (*Pharm. Rundschau*, **12**, 142).

[2] *Arch. Pharm.*, *1885*, 611.

[3] K. Kippenberger, 1895: *Ztschr. anal. Chem.*, **34**, 317; **35**, 407, 422.

to have obtained the lower periodides, at least in part, in their methods of estimation. The last-named author proceeded upon a volumetric deduction of a general formation of triiodides, and sought to so vary the conditions as to support the factor of a triiodide. In 1896, Gomberg,[1] along with his production of caffeine perhalides above referred to, established the volumetric estimation of caffeine in acidulated solutions as a pentaiodide, and this was used, with a method of extraction from Kola, throughout the work of Mr. Knox and one of us[2] upon the caffeine compound of kola, with complete satisfaction.

THE HIGHER PERIODIDES IN RESPECT TO CONSTANCY OF COMPOSITION.

The number of the periodides of pyridine is representative of the fact that most of the alkaloids of pyridine-derived constitution will form each more than one periodide, according to conditions. We find it is more expedient to secure the exclusive formation of the higher periodide, by needful conditions, than that of any other periodide obtainable. The higher periodides are not surpassed in completeness of precipitation, and they are sufficiently stable. At least this is true of those alkaloids included in this report. In future reports we desire to be able to give analyses of all the readily obtained periodides of each of the alkaloids reported upon in this article.

If we add the iodopotassium iodide solution to the solution of an alkaloidal salt, keeping from the beginning to the end the alkaloid in excess, it is generally the lowest periodide (in most cases a triiodide) that is formed, but if the order be reversed and the alkaloidal solutions added to the iodopotassium iodide solution, keeping all the time a large excess of iodine, it is generally the highest periodide that is formed. We have found this rule to hold good with atropine, strychnine, brucine, aconitine, and several other alkaloids. It was mainly the lower periodides of alkaloids that were made and described by Jörgensen; they are generally very stable and can be easily obtained in crystalline form by crystallization from some suitable solvent. As to the higher periodides, some of them are stable enough to be

[1] This Journal, 18, 331.

[2] Knox and Prescott: *Proc. Am. Pharm. Assoc.*, 44, 128; 45, 131; This Journal, 19, 63; 20, 34.

recrystallizable; many others are easily decomposed in solution into free iodine and lower periodides. Atropine enneaiodide belongs to the first class; strychnine heptaiodide and brucine heptaiodide belong to the second.

Following the above-mentioned rule, we have succeeded in obtaining an enneaiodide of atropine, $C_{17}H_{23}NO_3HI.I_8$; a heptaiodide of strychnine, $C_{21}H_{22}N_2O_2HI.I_6$; a heptaiodide of brucine, $C_{23}H_{26}N_2O_4HI.I_6$, and, as it is probable, a triiodide and a heptaiodide of aconitine. The tetraiodide of morphine, obtained by Jörgensen, is the only periodide of morphine that we have been able to make by precipitation.

These compounds are of the common order of alkaloidal hydriodide periodides. The single atom of iodine in the normal hydriodide is transposed by silver nitrate solution with precipitation, but does not respond to reducing agents. The rest of the iodine, being additive to the first atom of this element, is very easily taken up by reducing agents, such as sulphur dioxide, a thiosulphate, or powdered zinc.

PREPARATION OF THE HIGHER PERIODIDES IN PURITY FOR ANALYSIS.

The periodides, of which analysis is given in this paper, were all made according to the following method: One gram of the alkaloid was dissolved in about 200 cc. of water acidulated with sulphuric or hydrochloric acid, and the solution poured, in small quantities at a time, into 500 cc. of water containing one per cent. free iodine and one and a half per cent. potassium iodide. After shaking until the liquid became perfectly clear, the mother-liquor was removed in filtration by means of a pump, the precipitate well washed with cold water and dried first on porous plates and then in a vacuum over sulphuric acid. For the aconitine triiodide the order of mixing was reversed, and an excess of aconitine kept during the whole operation. After drying, the precipitate was recrystallized from alcohol. These periodides, so prepared, were subjected to analysis by the method given under atropine below, and as stated further under the several alkaloids, and from the results of the analysis, the volumetric factor of free iodine for each alkaloid was determined.

ATROPINE ENNEAIODIDE AND ITS ANALYSIS.

The enneaiodide, obtained as above described, is a very dark brown, almost black powder, quite permanent in dry air, and has only a slight odor of iodine. It is very difficultly soluble in ether, chloroform, benzene, or carbon disulphide, but is soluble in alcohol, very freely when hot. In cold water it is insoluble; hot water decomposes it quickly; it is also decomposed by concentrated solutions of potassium iodide. At 90° C. it commences to give up iodine vapors, and at 140° C. melts to a dark liquid. To obtain it in crystalline form it is first washed with a little cold alcohol to remove traces of free iodine, and then dissolved in warm alcohol. On cooling it crystallizes out in dark-green prisms and leaflets, having the same properties as the non-crystallized body. In analysis we estimated the additive iodine volumetrically, and the total iodine both gravimetrically and volumetrically.

To estimate the additive iodine a small quantity of the enneaiodide is dissolved in very little alcohol, an excess of a standardized solution of sodium thiosulphate added, and the excess titrated back with a standard solution of iodine, using starch as the indicator.

For total iodine the substance is covered with an excess of powdered metallic zinc and some water, and then boiled gently for ten or fifteen minutes, taking care to prevent loss by spurting; the mixture is then thrown upon a filter, and the containing flask and the filter are thoroughly washed with hot water. The iodine in the zinc iodide thus formed can either be estimated by precipitation with silver nitrate and nitric acid and weighing as silver iodide, or it is precipitated with an excess of a standardized solution of silver nitrate and the excess titrated back with a standard solution of ammonium thiocyanate, using ferric nitrate as indicator.

In the following analyses the standard silver nitrate solution was made to correspond with one per cent. of iodine, and the ammonium thiocyanate solution to correspond, cc. per cc., with the silver nitrate solution. The standard solution of iodine contained one per cent. of iodine, and the sodium thiosulphate solution corresponded, cc. per cc., with the iodine solution.

Analysis of the atrophine enneaiodine not recrystallized: In the

volumetric estimation for total iodine, 0.15225 gram required 12.2 cc. of the silver nitrate solution. For the iodine removed by reduction, 0.19255 gram required 13.7 cc. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_3.HI.I_8$.	Found.
Iodine by reduction	70.88	71.15
Total iodine	79.74	80.13

In the gravimetric estimation from 0.218 gram 0.3207 gram silver iodide was obtained.

	Calculated for $C_{17}H_{23}NO_3HI.I_8$.	Found.
Total iodine	79.74	79.48

Analysis of the atropine enneaiodide recrystallized from alcohol.— The methods employed were the same as with the non-recrystallized compound, and the standard solutions of the same strength.

In the volumetric estimation of total iodine, 0.12685 gram required 10.1 cc. of the silver nitrate solution. For the iodine removed by reducing agents, 0.23105 gram required 16.4 cc. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_3.HI.I_8$.	Found.
Total iodine	79.74	79.62
Iodine by reduction	70.88	70.98

In the gravimetric estimation of total iodine, 0.2031 gram gave 0.30035 gram silver iodide.

	Calculated for $C_{17}H_{23}NO_3.HI.I_8$.	Found.
Total iodine	79.74	79.90

The constitution of the compound is that of atropine hydriodide octaiodide. The alkaloidal hydriodide is formed, in the (acidulated) solution, by transposition of the alkaloidal salt taken with potassium iodide. Thus: $C_{17}H_{23}NO_3.HCl + KI + I_8 = C_{17}H_{23}NO_3.HI.I_8 + KCl$.[1] Therefore the ratio of the free iodine consumed, to the absolute atropine, is the ratio of I_8 to $C_{17}H_{23}NO_3$, equal to ratio 1012.24 to 288.38, or of 1 of iodine to 0.2849 of atropine.[2] And 1 cc. of decinormal iodine solution consumed is equivalent to 0.0036048 gram of the atropine. *This decinormal*

[1] For experimental verification of this equation, see a later paragraph in this paper.

[2] The atomic weights taken were those of L. Meyer and K. Seubert, H = 1.

factor was found to hold good under the control estimations reported further on.

OTHER ATROPINE PERIODIDES, AND ATROPINE MERCURIC IODIDES.

Having obtained the enneaiodide of atropine, it was natural to suppose the existence of a heptaiodide, with probability of a complete series from the triiodide to the enneaiodide. And in fact in the course of our work we once obtained this heptaiodide. But our efforts to determine the exact conditions necessary for the formation of this body have so far not been successful. Whether additional quantities of atropine will make the precipitate take up more atropine and become a lower periodide we shall try to determine by later experiments. On the other hand, when the order is reversed and the iodine solution is added to the atropine solution, it is always a lower periodide that is formed; but whether on continued addition of the iodine the precipitate will take up more of it and become a higher periodide, we cannot say as yet.

The easiest way to obtain the periodides of atropine is to use chloroform as a solvent. On adding twenty grams atropine to a warm solution of thirty grams iodine in chloroform (500 cc.) the enneaiodide crystallizes out very soon in the shape of small, shining, dark green crystals. If these be removed by filtration, the mother-liquor will give several successive crops of the dark blue pentaiodide, and at last a crop of the brownish-red triiodide.

Atropine mercuric iodides are best known as products of precipitation of atropine salts by Mayer's reagent, the solution of potassium mercuric iodide.[1] We find that they can be obtained by shaking the alcoholic solution of a periodide with metallic mercury and warming the mixture. Double iodides of atropine and mercury can also be made by mixing theoretical quantities of atropine and iodine, adding a little alcohol and an excess of mercury, slightly warming, and shaking till the color of iodine disappears. If the higher periodides of atropine be used in the preparation of this double iodide of atropine and mercury there

[1] Groves, 1859: *Quar. J. Chem. Soc.*, **11**, 97, 188. F. F. Mayer, 1862: *Am. J. Pharm.*, **35**, 20; *Chem. News*, **7**, 159; **8**, 177, 189. Prescott, 1880.: *Am. Chem. J.*, **2**, 294; **14**, 606.

is always separation of mercurous iodide; but if theoretical quantities of atropine and iodine be used there is no separation of mercurous iodide. The formula of this double iodide of mercury and atropine, as shown by our analysis, seems to be $C_{17}H_{23}NO_3.HI.HgI_2$. It resembles in composition several other double iodides of alkaloids and mercury obtained by Groves by a different method, and agrees in proportion with the strychnine compound, not with the morphine or quinine compound obtained by one of us in 1880.[1] But besides this double iodide we also obtained another having the composition $(Atrop.\ HI)_2.HgI_2$. It was made by treating a solution of the $(Atrop.\ HI).HgI_2$ in diluted alcohol with an excess of potassium iodide. From the liquid obtained by shaking an alcoholic solution of atropine and iodine with mercury the monoatropine hydriodide mercuric iodide crystallizes out in shining, yellow crystals, melting at 80° to 90° C., difficultly soluble in ether or chloroform, partly soluble in hot water, and very soluble in warm alcohol. The diatropine hydriodide mercuric iodide obtained, as said above, by the action of potassium iodide on the mono compound, crystallizes in perfectly white, silky needles, which, on being dried, assume a yellowish tint. They melt at 98° to 99° C., are very easily soluble in warm alcohol, and quite soluble in hot water.

The analysis for mercury and for iodine in these bodies can be made in different ways, but the best results are obtained by a modification of the method of Risse.[2] The mercury and the iodine are determined in two separate portions. For mercury the substance is dissolved in a little warm alcohol and a little water added; the solution is then acidulated with a few drops of dilute hydrochloric acid and saturated with hydrogen sulphide. The mercuric sulphide is then dried and weighed in the usual way. For the determination of iodine the substance is treated with a hot solution of potassium hydroxide (1 : 10), diluted with water, filtered, and when completely cold, neutralized with acetic acid. The iodine is now precipitated with silver nitrate and nitric acid, and determined as silver iodide in the usual way.

In the following analyses the standard silver nitrate solution

[1] Prescott: *Am. Chem. J.*, 2, 297.
[2] *Ann. Chem.* (Liebig), 107, 223.

was made to correspond with one per cent. of iodine, and the ammonium thiocyanate solution to correspond, cc. per cc., with the silver nitrate solution. The standard solution of iodine contained one per cent. of iodine, and the sodium thiosulphate solution corresponded, cc. per cc., with the iodine solution.

Analyses of the Double Salts of Atropine Hydriodide and Mercuric Iodide: 0.2632 gram of the monoatropine hydriodide mercuric iodide gave 0.0699 gram mercuric sulphide, and 0.30445 gram of the substance gave 0.24785 gram silver iodide.

	Calculated for $C_{17}H_{23}NO_3.HI.HgI_2$.	Found.
Mercury	23.03	22.89
Iodine	43.74	43.98

Of the diatropinehydriodide mercuric iodide, 0.1798 gram gave 0.032 gram mercuric sulphide, and 0.257 gram of the substance gave 0.18885 gram silver iodide.

	Calculated for $(C_{17}H_{24}NO_3.HI)_2HgI_2$.	Found.
Mercury	15.58	15.34
Iodine	39.46	39.70

STRYCHNINE HEPTAIODIDE AND ITS ANALYSIS.

The heptaiodide of strychnine is a dark brown powder, hardly soluble in ether, chloroform or benzol, and requires considerable alcohol for solution. It cannot be recrystallized, as it is easily decomposed into free iodine and the triiodide.[1]

The total iodine was determined by silver nitrate after reduction with zinc and ammonia. The additive iodine was estimated after dissolving the periodide in alcohol, by titrating with thiosulphate.

For total iodine:

1. 0.3816 gram of the periodide gave 0.51345 gram silver iodide.
2. 0.30625 gram gave 0.4112 gram silver iodide.

	Calculated for $C_{21}H_{22}N_2O_2\,HI.I_6$.	Found.
1	72.66	72.70
2	....	72.54

For additive iodine:

1. 0.1754 gram of the substance was found to contain 0.109 gram free iodine.

2. 0.17805 gram contained 0.111 gram free iodine.

[1] A triiodide was reported by Tilden in 1865 (see Geuther's lists, *loc. cit.*).

	Calculated for $C_{21}H_{22}N_2O_2.HI.I_6$.	Found.
1	62.28	62.14
2	....	62.34

Six atoms iodine coming from the free iodine of the iodo-potassium iodide solution, we get the ratio: I_6 to $C_{21}H_{22}N_2O_2$, or 1 of iodine to 0.439 of strychnine absolute. This gives the *decinormal factor* (the value of one cc. of decinormal iodine solution) as 0.0055547 for strychnine.

BRUCINE HEPTAIODIDE AND ITS ANALYSIS.

This was made according to the general method already given, by pouring a half per cent. solution of brucine acidulated with hydrochloric acid into a large excess of a one per cent. solution of iodine. In appearance and solubility it closely resembles the heptaiodide of strychnine, but it exercises a strong reducing action on silver salts, so that its analysis for total iodine is best accomplished by the aid of nitrous acid and bisulphide of carbon as described under the head of morphine tetraiodide and its analysis.

For total iodine:

1. 0.1916 gram of the periodide was found to contain 0.13229 gram total iodine.

2. 0.2395 gram of the periodide contained 0.16536 gram total iodine.

	Calculated for $C_{23}H_{26}N_2O_4.HI.I_6$.	Found.
1	69.21	69.04
2	....	69.04

For additive iodine:

1. 0.1622 gram of the substance contained 0.096006 gram free iodine.

2. 0.192 gram contained 0.114 gram free iodine.

	Calculated for $C_{23}H_{26}N_2O_4.HI.I_6$.	Found.
1	59.32	59.19
2	....	59.37

For brucine, therefore, the ratio is I_6 to $C_{23}H_{26}N_2O_4$, or 1 of iodine to 0.5179 of anhydrous brucine. And 1 cc. of strictly decinormal solution of iodine indicates 0.0065530 of brucine, *the decinormal factor*, subjected to trial as stated later.

MORPHINE TETRAIODIDE AND ITS ANALYSIS.

Two samples were made. In the first, one gram of morphine

dissolved in 200 cc. acidulated water was added to a solution of five grams iodine and seven and one-half grams potassium iodide in 500 cc. water, the mixture shaken till the supernatant liquid was perfectly clear, and the precipitate washed and dried in vacuum. In the second, two grams iodine and three grams potassium iodide were dissolved in 200 cc. water and the solution poured slowly into a solution of morphine containing three grams morphine in 600 cc. acidulated water. The analysis, as given below, showed that the precipitate in both cases was the same; namely, $C_{17}H_{19}NO_3HI.I_3$. This compound, morphine tetraiodide, was made known by Jörgensen in 1870.[1] We find it to be the only periodide formed by morphine under any of the conditions of this precipitation from aqueous solutions.[2] It is notable that in this periodide the base as a monamine holds an even number of atoms of total iodine. The periodide precipitate of morphine is practically insoluble when the iodine is in excess, though appreciably soluble when the morphine is in excess, as it is in pure water, the more so if strongly acidulated.

In the analysis of the morphine periodide, the precipitate is to be collected and quickly washed with water by the aid of the pump, and then dried in vacuum over sulphuric acid to a constant weight. The additive iodine is readily determined, in a weighed portion, by dissolving in alcohol and titrating with a standard solution of sodium thiosulphate as stated in previous paragraphs. The total iodine determination in this compound gives special difficulty, as neither the sulphur dioxide nor the powdered zinc, previously used in this laboratory for analytical reduction of periodides, works well with morphine periodide, but the following procedure suffices. The periodide is covered with powdered zinc and stronger water of ammonia and set aside half an hour, the mixture is then heated on the water-bath till all the ammonia is driven off, avoiding loss by spurting. A little water is now added and the mixture boiled about ten minutes. The whole is filtered into a separator of about 500 cc.

[1] *J. prakt. Chem.* (2), **2**, 437.

[2] The present hypothesis of structure of periodides would imply, therefore, that the compound is a dimorphine octaiodide (This Journal, **17**, 780; **19**, 331). A lower periodide of morphine was obtained by evaporation of an alcoholic solution containing excess of morphine, by H. R. Bauer (*Arch. Pharm.* [3], **5**, 289-309).

capacity, the excess of zinc well washed with hot water, and water added to make 200 or 300 cc. When perfectly cold, the mixture is acidified slightly with very dilute sulphuric acid, then twenty cc. of carbon disulphide are poured into the separator, and ten to twelve drops of concentrated sulphuric acid *saturated with nitrous acid* are added. The separator is closed and shaken, and the solution of iodine in carbon disulphide carefully run out upon a wetted filter. Fresh carbon disulphide is added in the separator and the separation repeated till all the iodine is removed. The iodine is now washed on the filter, first with water, then with a very weak solution of sodium bicarbonate. It is then run into a flask, and thirty cc. of a solution of sodium bicarbonate, five grams to the liter, are added. Finally the iodine is titrated with the standard solution of sodium thiosulphate. The results were as follows :

I. Iodine in excess :

0.2692 gram gave 0.13 gram additive iodine and 0.2732 gram gave 0.174311 gram total iodine.

	Calculated for $C_{17}H_{19}NO_3.HI.I_2$.	Found.
Additive iodine	48.02	48.29
Total iodine	64.03	63.80

II. Morphine in excess.

0.3155 gram were found to contain 0.152832 gram additive iodine and 0.2708 gram contained 0.172076 gram total iodine.

	Calculated for $C_{17}H_{19}NO_3.HI.I_2$.	Found.
Additive iodine	48.02	48.44
Total iodine	64.03	63.54

For morphine the ratio is I_2 to $C_{17}H_{19}NO_3$, or ratio of 379.59 to 284.38, that is 1 of free iodine consumed to 0.74918 of morphine, anhydrous. And one cc. of strictly decinormol solution of iodine corresponds to 0.0094794 gram of morphine.

ACONITINE HEPTAIODIDE (?) AND ITS ANALYSIS.

The alkaloid we used was obtained from Merck and marked "From Acontum Napellus, crystallized, pure." This periodide was made according to the general plan of obtaining the highest periodide of an alkaloid.

For additive iodine 0.2588 gram contained 0.126886 gram free

iodine and 0.1471 gram contained (by nitrous acid method) 0.082271 gram total iodine.

	Calculated for $C_{33}H_{45}NO_{12}.HI.I_6$.	Found.
Additive	49.58	49.03
Total	57.85	55.93

We make our calculations upon the aconitine formula of Dunstan.[1] The formula of Freund[2] though distinctly different in constitution, gives but slightly different molecular weight. Other proposed formulas approach the same molecular weight. $C_{34}H_{47}NO_{11} = 643.55$ (Freund). $C_{33}H_{45}NO_{12} = 645.54$ (Dunstan). $C_{33}H_{47}NO_{12} = 647.54$ (Jürgens). $C_{33}H_{43}NO_{12} = 643.54$ (Wright and Luff).

An insufficiency of the aconitine in our hands prevented our making duplicate estimations. With both the higher and the lower periodide, it is to be seen that the total iodine found is somewhat too low for the calculated quantity of this element, calculating for heptaiodide and triiodide, respectively. The additive iodine in both cases falls below calculation, but not enough below to discredit the formulas. When we return to these estimations with a larger supply of the alkaloid we shall find whether the instability of aconitine will prevent constant results in analysis of the higher periodide or not.

ACONITINE TRIIODIDE (?).

This was made by adding a one per cent. solution of iodine to an acidulated solution of aconitine, leaving the latter in excess, and recrystallizing the precipitate from alcohol. Thus obtained it forms beautiful brown-red crystals, very soluble in alcohol, insoluble in water and hardly soluble in ether, benzol, or chloroform. Melting-point 211°–212° C.

For additive iodine :

0.01773 gram of the substance contained 0.042352 gram free iodine.

Calculated for $C_{33}H_{45}NO_{12}.HI.I_2$.	Found.
24.69	23.89

For total iodine by the aid of nitrous acid and bisulphide of carbon, as given under the head of morphine.

[1] *J. Chem. Soc.*, 67, 459.

[2] *Ber. d. chem. Ges.*, 27, 722.

0.2111 gram contained 0.07505 gram total iodine.

Calculated for $C_{23}H_{45}NO_{12}.HI\ I_2$.	Found.
37.03	35.56

VERIFICATION OF THE EQUATION FOR THE IODINE FACTOR.

Partly from the fact that Kippenberger[1] has proposed a different reaction in the formation of periodide precipitates, and for other reasons, we thought it advisable to prove irrefutably that the iodide of potassium of the iodine solution takes an active part in the reaction by which the atropine enneaiodide, as an example, is formed and gives off an amount of iodine which is just equal to the amount of the normal iodine of the enneaiodide.

We proceeded in the following manner: We first determined the strength of our iodine solution with regard to free iodine; this was done by means of a sodium thiosulphate solution of known strength. We then took ten cc. of this iodine solution and determined the total amount of iodine, free as well as bound to potassium, by shaking them in a flask with an excess of powdered metallic zinc till the color of iodine disappeared, filtering the solution of zinc iodide and potassium iodide thus obtained, washing the flask and the excess of zinc with hot water and precipitating the iodides in the filtrate with silver nitrate and nitric acid. From the weight of silver iodide washed and dried in the usual way, we calculated the amount of total iodine present in our iodine solution. By subtracting the amount of free iodine from that of the total iodine we obtained the amount of iodine present in our solution as potassium iodide. We thus found that the iodine solution contained one per cent. free iodine and 1.2312 per cent. combined iodine.

We then put forty cc. of this iodine solution in a 100 cc. measuring flask, added twenty cc. of a three-tenths per cent. solution of atropine alkaloid, and after shaking well, diluted the liquid in the flask to 100 cc. We now took two vials and in each filtered off twenty-five cc. from the flask. In the first vial, the amount of free iodine titrated back with sodium thiosulphate was found to be 0.0465. From this it is easy to deduce that the twenty cc. of the three-tenths per cent. atropine solution consumed 0.214

[1] *Ztschr. anal. Chem.*, 35, 10; 34, 317. On this question also see Gomberg, 1896: This Journal, 18, 332.

gram of the free iodine. In the second vial the total iodine was determined in the same way as described above, and the quantity of silver iodide was found to be 0.3023 gram, which shows that after the treatment with atropine the liquid contained 1.633 per cent. total iodine. From these data we deduce that the twenty cc. of the atropine solution have taken up 0.02528 gram iodine from the bound iodine. As the twenty cc. of atropine solution contained 0.06 gram atropine we find for 100 parts of precipitated enneaiodide

	Found. Per cent.	Calculated. Per cent.
Atropine	20.05	20.26
Iodine taken from the free iodine of the iodine solution	71.50	70.88
Iodine from the iodine bound as KI	8.45	8.86

We see that in aqueous acidulous solutions the potassium iodide takes an active part in the reaction by joining in a yield of hydriodic acid for the normal hydriodide of the alkaloid, necessary to hold the additive iodine of the periodide. When carbon disulphide or carbon tetrachloride is used as a solvent for the atropine and the iodine, no periodide seems to be formed, possibly for the reason of there being no generation of hydriodic acid for the making of hydriodide. As to the formation of the periodides in chloroformic solution of atropine and iodine, it might possibly be explained by the substituting action of iodine either upon the chloroform or upon a side-chain of the atropine.

The direct substitution of iodine for some of the hydrogen in these bodies might, in this case, be made possible by the presence of the natural base, which combines with the hydriodic acid when formed by such a substitution. Part of the atropine would then act in a manner similar to that of mercuric oxide, which is usually employed in the iodizing of hydrocarbons. An analogous case we have in the easy substitution of iodine for some of the hydrogen in aniline, a part of which combines with the hydriodic acid, which is set free through the substitution of iodine for hydrogen in another part. At any rate we shall endeavor to determine the by-products formed when atropine enneaiodide is produced in chloroformic solutions.

PROCEDURE IN THE VOLUMETRIC METHOD.

The general mode of procedure in the estimation of the strength of an aqueous solution of an alkaloidal salt is as follows: To about ten cc. of decinormal iodine solution diluted with a little water, one cc. of the acidulated alkaloidal solution is added, and the mixture well shaken for a few minutes. Should the precipitate separate out very quickly, and the clear supernatant liquid have only a light yellow or greenish color, or be altogether colorless, the alkaloidal solution is too strong and must be diluted, till after a few trials the clear supernatant liquid retains a very dark red color after the separation of the precipitate. The acidulated alkaloidal solution is then made up to a given volume, and ten or fifteen cc. of it are run from a burette into a graduated vessel, into which has been previously put twenty-five or thirty cc. decinormal iodine solution diluted with a little water. The mixture is then made up to a given volume and shaken till the supernatant liquid is perfectly transparent, and is of a very dark red iodine color. This point is very important, and should the clear liquid not have this dark red color, the experiment with most alkaloids (except morphine and possibly some others) should be repeated, putting more decinormal iodine into the graduated vessel, or decreasing the number of cc. of the alkaloidal solution. It would not do to add more decinormal iodine to the same mixture, as the iodine must be in large excess during the whole operation, in order to prevent the formation of lower periodides, which once formed, might not take up fresh iodine and form higher periodides. Only with morphine, which in such solutions forms but one periodide, these precautions are unnecessary. When the liquid has become perfectly clear, an aliquot portion of it is filtered off, and the excess of iodine determined by standard sodium thiosulphate. From these data are obtained the quantity of iodine consumed. This quantity of iodine, multiplied by the "ratio of alkaloid to 1 of iodine," gives the quantity of alkaloid sought. If preferred, but generally with less convenience to the chemist, the number of cubic centimeters of decinormal solution of iodine consumed may be multiplied by the "alkaloidal factor of 1 cc. $\frac{N}{10}$ I sol."

VERIFICATION OF THE IODINE FACTORS BY VOLUMETRIC CONTROL.

For Atropine.—In the following estimations of the strength of atropine solutions, both the iodine solution and the sodium thiosulphate solution were strictly decinormal. Of the iodine solution twenty or twenty-five cc. were put into a 100 cc. measuring flask and atropine solutions of known strength run in from a burette, and the operation continued as described above. When the supernatant liquid was perfectly transparent the flask was filled up to 100 cc. and fifty cc. were filtered off. In these fifty cc. the excess was determined by means of the tenth-normal thiosulphate solution, and the strength of the atropine solutions calculated by using the factor 0.0036048 for every cubic centimeter of decinormal iodine used up.

	Actual strength. Per cent.	Number of cc. of the atropine solution taken.	Number of cc. of the tenth-normal iodine used up.	Results in strength. Per cent.
1	0.50	12	15.6	0.47
2	0.40	15	14.9	0.36
3	0.30	17	13.2	0.28
4	0.25	12	10.0	0.28

For Strychnine.—To test the correctness of the ratio of 1 of free iodine to 0.4390 of strychnine, two solutions were prepared, one of one per cent., the other of 0.612 per cent. of the alkaloid. The estimations, by the volumetric method, gave results as follows:

	Actual strength. Per cent.	Strychnine solution taken. cc.	Iodine consumed.	Results obtained. Per cent.
1	1.0	3	0.07$_6$	1.026
2	0.612	7	0.191	0.633

For Brucine.—Two solutions of the alkaloid were made, and estimated volumetrically, calculating by the ratio 1 part of iodine to 0.5179 part of anhydrous brucine, with these results:

	Actual strength. Per cent.	Brucine solution taken. cc.	Iodine consumed.	Results obtained. Per cent.
1	1.0	10	0.193	0.999
2	0.5	10	0.096	0.497

For Morphine.—Three standard solutions were made of strengths in anhydrous alkaloid as below tabulated. This was done by weighing a good article of well-crystallized morphine,

free alkaloid, as $C_{17}H_{19}NO_3.H_2O$. The results were calculated by the ratio 1 of iodine to 0.74918 of morphine, absolute.

	Strength in per cent.	Morphine solution. cc.	Iodine solution. cc.	Iodine consumed.	Result in per cent.
1	0.518	10	20	0.070116	0.525
2	0.259	10	20	0.034272	0.257
3	0.100	10	20	0.014020	0.105

THE IODINE FACTORS OF THE ALKALOIDS SO FAR DETERMINED.

Higher periodide formed.	Ratio of alkaloid to one of iodine.	Alkaloid factor of one cc. tenth-normal iodine solution.
Atropine, $C_{17}H_{23}NO_3.HI.I_8$	0.2849	0.0036048
Strychnine, $C_{21}H_{22}N_2O_2.HI.I_6$	0.4390	0.00555467
Brucine, $C_{23}H_{26}N_2O_4.HI.I_6$	0.5179	0.00655299
Morphine, $C_{17}H_{19}NO_3.HI.I_3$	0.74918	0.00947937
Aconitine, $C_{33}H_{45}NO_{12}.HI.I_6$	.....	.....
By Gomberg in 1896 :[1]		
Caffeine, $C_8H_{10}N_4O_2.HI.I_4$	0.3834	0.00485

APPLICATION IN ASSAY OF CRUDE MEDICINAL DRUGS.

We have made estimations of total alkaloids in nux vomica, and in belladonna, by the periodide volumetric method, after extraction of the alkaloid in several ways, and have obtained satisfactory results. We have work in hand by which we hope to reach more expeditious methods of extraction. Among the menstrua under experimentation, are a saturated solution of gaseous ammonia in ether, a chloroformic solution of ammonia,[2] and similar agents.

A VOLUMETRIC ASSAY OF OPIUM.

The morphine was estimated as periodide, after successive treatment with benzol, amyl alcohol or acetone, and lime-water.

This method proceeds upon the following plan: The opium alkaloids are set free by action of ammonia with certain solvents. The free narcotine, papaverine, codeine, and thebaine are then removed by percolation with benzene, after which the morphine is taken out by percolation with acetone,[3] in which the morphine

[1] This Journal, 18, 339.

[2] Suggested by Siedler and Thoms: *Ber. d. pharm. Ges., 1898*, 28.

[3] Instead of acetone there may be used pure amyl alcohol, boiling between 128° and 132° C., and leaving no residue upon evaporation below the boiling-point.

is sufficiently soluble. The acetone is then evaporated off, and the residue taken up with lime-water, which completely dissolves and purifies the morphine. It remains to filter the lime solution, acidulate it with hydrochloric acid, and estimate the morphine as periodide by titration as already detailed in this paper.

In the percolation of the opium with different solvents to separate the morphine, we depend upon two things, (1) the preparing of the opium powder by digestion with the ammonia and the solvents and then drying, and (2) an admixture with dried common salt in transferring to the percolator.

The Materials for the Assay.—Opium in fine powder (No. 60 or finer), one gram; stronger ammonia water; alcohol, ether, chloroform, pure benzene (crystallized); acetone, boiling between 54° and 58° C., about 200 cc.; some good lime-water; ordinary common table salt, about twenty grams; some diluted hydrochloric acid (ten per cent.); decinormal solution of iodine with potassium iodide (Wagner's reagent), and sodium thiosulphate solution standardized with the solution of iodine.

Directions for the Assay.—Of the opium in fine powder one gram is weighed into a small mortar or deep dish, such as can be well covered with admission of a small pestle.[1] A mixture is made of five cc. of stronger ammonia water, five cc. of alcohol, twenty cc. of ether, and ten cc. of chloroform. The opium is rubbed up with two or three cc. of this mixture, to make a uniform paste, using a pestle that can be left in the dish when it is covered. The covered dish is now put aside for about three hours, from time to time moving the dish gently; about fifteen grams of well dried and finely powdered common salt are now added and carefully mixed into the mass. Then the dish is left open in a warm place, of 30° to 35° C., for two or three hours, when it is placed in a desiccator containing sulphuric acid and a dish of paraffin, a vacuum desiccator being preferable, until the mixture is perfectly dry as shown by the looseness of the powder under the motion of the pestle. If left over night it is sufficient. The entire contents of the dish are now transferred to a little glass percolator of about one and three-tenths centimeters

[1] A screw-top ointment jar of mortar-shaped bottom and four or six ounces capacity serves very well.

(one-half inch) inner diameter and twenty-two centimeters (nine inches) length,[1] rubbing out the dish twice with a little more of the dried common salt. The mass is now percolated with the benzene, until the percolate is colorless, and until upon evaporating one or two drops of the percolate in a watch-glass, taking up the residue with four or five drops of acidulated water and adding a drop or two of Wagner's reagent, no turbidity appears (removal of alkaloids other than morphine). A shallow dish is now set under the percolator, and pure acetone used to continue the percolation to complete exhaustion, as found by evaporating ten drops of the percolate on a watch-glass, taking up the residue with two or three drops of acidulated water, and adding a drop or two of Wagner's reagent, when no turbidity at all should appear. Usually as much as 200 cc. of acetone are required. The acetone is now evaporated, at a temperature not exceeding 45° C., to complete dryness. The residue when cool is rubbed up with good fresh lime-water, the solution poured without filtering into a graduated stoppered cylinder of 100 cc., the dish washed four or five times with portions of lime-water, to fully clean the dish, when lime-water is added to make the volume 100 cc. The cylinder is now securely stoppered and well shaken for half an hour. Of the mixture enough is now filtered into another graduated cylinder, with glass stopper, to make up a filtrate exactly fifty cc. To this liquid is added diluted hydrochloric acid (ten per cent.) to just perceptible acidulation, and the tenth-normal iodine solution is slowly run in from the burette while gently shaking the cylinder until precisely twenty-five cc. have been added. Water is added to any convenient mark of the cylinder, which is then stoppered securely and shaken vigorously and continuously (for about twenty minutes) until, on standing a minute or two, the supernatant liquid (of a pronounced iodine-red color)[2] is perfectly clear and transparent. The liquid is now filtered off so as to take just one-half the volume of the filtrate. In this half of the liquid the excess of iodine is titrated back with the tenth-normal sodium thiosulphate solution, using starch as an indicator. The number of cubic centimeters of the thiosulphate solution multiplied by two,

[1] The tube of a one-ounce syringe does very well.

[2] If the liquid does not have this red color, it must be because of a lack of the indispensable excess of the iodine, of which an additional quantity should be added.

is subtracted from twenty-five, the number of cubic centimeters of iodine solution used. The remainder is now multiplied by the factor 1.89586 (0.0094793 × 2 × 100), the product being the percentage of morphine in the powdered opium as weighed.

The precautions most essential are (1) that the opium residue before percolation be thoroughly dried, (2) that the acetone should not contain anything distilling below 54° C., or above 58° C., and (3) that after the added excess of iodine the container be continuously shaken until the precipitate is so fully separated that the solution above it is clear. An automatic shaker is an aid in this assay. A second estimation can be made with the remaining part of the lime solution.

Without the use of lime-water in purification of the morphine of the residue, we find the color of the resulting acidulous solution to be inconvenient in the titration, and find the percentage figure to be uniformly higher than when obtained after lime solution. The vessel is easily cleaned from adhering morphine periodide by the use of acetone.

RESULTS OF THE OPIUM ASSAY BY THE PERIODIDE METHOD.

We can give here the results of assays of but three samples of powdered opium, these coming from three different reputable houses. They were all marked, sample A to contain fourteen per cent., samples B and C to contain the quantity required by the U. S. P. Three analyses of each sample were made, and to sample A the U. S. P. method was also applied, and was found to contain 14.4 per cent. morphine by that method. The volumetric method was carried out exactly as described above.

SAMPLE A.

	Opium taken in grams.	Iodine consumed by one-half.	Percentage morphine found.
1	1.0036	0.116644	17.41
2	1.008	0.116732	17.37
3	1.0022	0.116642	17.44

SAMPLE B.

	Opium taken in grams.	Iodine consumed by one-half.	Percentage morphine found.
1	1.0033	0.08872	13.25
2	1.0023	0.08872	13.20
3	1.0026	0.08872	13.21

SAMPLE C.

	Opium taken in grams.	Iodine consumed by one-half.	Percentage morphine found.
1	0.9969	0.096319	14.48
2	1.0016	0.097219	14.55
3	0.9988	0.094552	14.19

AS A VALUATION OF THE MORPHINE OF ANY PHARMACOPOEIAL ASSAY.

If it should be desired to estimate the alkaloid in the crystals obtained in assay by the pharmacopoeia of this or any other country, the periodide volumetric analysis could be well applied as follows:

Let the crude morphine obtained by the pharmacopoeial method be taken up with lime-water, the latter made up to a given volume, and a measured portion of the filtered solution, placed in a graduated vessel and acidulated with hydrochloric acid; let a definite excess of the decinormal iodine be added, in small portions at a time, and shaken after each addition, till the periodide separates out, and the clear liquid retains a dark red color, making up the mixture to a given volume, filtering off half and then titrating the excess of iodine in this half by standard sodium thiosulphate, the amount of iodine consumed can be easily found. Working on ten grams opium, a tenth portion of the lime-water solution would represent one gram of opium, and the percentage of morphine would be equal to the weight of iodine consumed, multiplied by 74.918, or to the number of cubic centimeters of the tenth-normal iodine consumed, multiplied by 0.94793. Several analyses could be made with the remaining part of the lime-water solution.

CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.
July, 1898.

NEW BOOKS.

A LABORATORY GUIDE IN QUALITATIVE CHEMICAL ANALYSIS. By H. L. WELLS, YALE UNIVERSITY. New York: John Wiley and Sons. pp. 189. Price $1.50.

In the first nine chapters the author endeavors to get the student to learn, by direct experiment and by numerous questions, how to distinguish and divide what are usually termed bases

into the five or six generally accepted analytical groups. The purpose appears to be to make the student think, and there is little doubt but that if he conscientiously pursues the course outlined he will not fail to gain a very fair knowledge of the general principles of analysis.

Sixteen pages are devoted to the study of the acid radicals, the student being as before urged to test and note his discoveries. Numerous excellent practical hints appear here and there, helpful even to the more advanced student.

Two chapters are given to the analysis of solids and the preparation of reagents.

Part II considers theory. It discusses, among others, the radicals and formulas, ionizations and ions, etc. In the latter connection the author remarks, "the circumstance that ionization takes place greatly simplifies inorganic chemical analysis."

About a dozen pages are devoted to sensible and helpful suggestions on equation writing.

Part III considers the descriptive portion, which in most texts dealing with analysis, receives first attention.

The author has aimed to lead the student into analysis without resorting to the mechanical habit, and in this book contributes much to obviate and keep out this evil. He accordingly deserves great credit for his effort. Earnest teachers, who believe in laying a good foundation in analysis, will appreciate it and give the little volume a hearty welcome.

EDGAR F. SMITH.

ERRATA.

In the August issue, page 557, line 9, for "ammonium bromoselenide" read "ammonium bromoselenate."

Page 567, line 10 from bottom, for "ammonium selenium bromoselenate" read "ammonium bromoselenate."

Page 578, line 8, for "forty" read "four."

BOOKS RECEIVED.

Bulletin No. 74. 1. The Chinch-bug. 2. Earthworms a Source of Gapes in Poultry. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. 29 pp.

Bulletin No. 75. Commercial Fertilizers. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. 18 pp.

Foods and Food Adulterants. Investigations made under direction of H. W. Wiley, chief chemist, with the collaboration of K. P. McElroy, W. H. Krug, T. C. Trescott, W. D. Bigelow, and others. Part Ninth.—Cereals and Cereal Products. Bulletin No. 13, Division of Chemistry, U. S. Department of Agriculture, Washington, D. C. vii + 206 pp.

Composition of Maize (Indian corn). Including the Grain, Meal, Stalks, Pith, Fodder, and Cobs. Compiled chiefly from the Records of the Division of Chemistry, by H. W. Wiley. Bulletin No. 50, U. S. Department of Agriculture, Division of Chemistry, Washington, D. C. 31 pp.

Experiments with Sugar-beets in 1897. By Harvey W. Wiley. Bulletin No. 50. U. S. Department of Agriculture, Division of Chemistry, Washington, D. C. 165 pp., with two maps.

Special Report on the Beet-sugar Industry in the United States. U. S. Department of Agriculture, Washington, D. C. 240 pp. with two maps.

Second Part of the Tenth Annual Report of the Storrs Agricultural Experiment Station, 1897. 148 pp. Storrs Agricultural Experiment Station, Storrs, Conn.

Explosive Materials. The Phenomena and Theories of Explosion and the Classification, Constitution, and Preparation of Explosives. By Captain John P. Wisser. New York: D. Van Nostrand Co. 1898. vi + 160 pp. Price 50 cents.

Strawberries. By L. C. Corbett. Bulletin No. 52. West Virginia Agricultural Experiment Station, Morgantown, W. Va. March, 1898. 23 pp.

Proceedings of the American Philosophical Society held at Philadelphia for Promoting Useful Knowledge. Vol. xxxvii, No. 157. July, 1898. Philadelphia: The American Philosophical Society, 104 South Fifth Street. 174 pp.

Commercial Fertilizers. Special Bulletin. Second Edition. H. A. Huston, State Chemist, Purdue University, Lafayette, Ind. 8 pp. and table.

Lehrbuch der anorganischen Chemie. Von Prof. Dr. H. Erdmann in Halle. Mit 276 Abbildungen und vier Farbigen Tafeln. Braunschweig: Friedrich Viewig und Sohn. 1898. xxvi + 756 pp. Large 8vo. Flexible cloth. Price M. 18.

Elements of General Chemistry with Experiments. By John H. Long, M.S., Sc.D. Chicago: E. H. Colegrove. 1898. 408 pp. Price $2.00.